

THE BEHAVIOUR OF SOLUBLE PETROLEUM PRODUCT
DERIVED HYDROCARBONS IN GROUNDWATER

Phase I

PACE Report No. 85-3

prepared for

Petroleum Association for Conservation
of the Canadian Environment
1202 - 275 Slater Street
Ottawa, Ontario

by

G.C. Patrick, C.J. Ptacek, R.W. Gillham, J.F. Barker
J.A. Cherry, D. Major, C.I. Mayfield, R.D. Dickhout
Institute for Groundwater Research
University of Waterloo

November 1985



NOTICE

No responsibility is accepted by PACE or any of its members concerned with the preparation, production or publication of this report for any statement therein or omission therefrom resulting in any loss, damage or injury whatsoever to any person using this report.



EXECUTIVE SUMMARY

Introduction

This report describes the progress made during the first year of a three-year study that is being undertaken to examine and characterize the physical and chemical factors that affect the migration of soluble components of petroleum products in groundwater regimes. Specific objectives of the study include assessments of: 1) small-scale methods for measuring adsorptive retardation, 2) the effects of biodegradation on transport and 3) the potential for biochemical remediation of contaminant plumes. The results will be useful for the assessment of groundwater contamination by water-soluble organics and in the implementation of remedial actions to limit or reduce such contamination. Direct benefits will include an evaluation of the natural processes that control contaminant movement, including the identification of critical parameters required to define such process and an assessment of the means of obtaining values for these parameters. An in situ tester for field measurement of sorption will be evaluated as will in situ remedial techniques using microbial degradation.

The experimental approach includes a field-scale injection test where dissolved constituents migrate under a natural gradient, as well as a variety of small-scale laboratory and field test procedures. A major component of the assessment procedure involves a comparison of predicted behaviour, based on the results of the small-scale tests, with the observed behaviour of the plume generated by the field injection experiment. The field injection experiment was conducted in a sandy hydrogeologic environment at the Canadian Forces Base, Borden, Ontario, and the small-scale experiments were conducted on geologic materials from that site. Solutes used in the tests included benzene, toluene, and xylene.

Small-Scale Retardation Tests

Adsorptive retardation was evaluated using four different methods: i) calculations of adsorption coefficients based on empirical relationships between properties of the chemicals (aqueous solubility and octanol-water partition coefficients) and the organic carbon content of the sediment, ii) by static batch equilibrium experiments, iii) by dynamic laboratory column experiments and iv) by a recently developed in situ field column procedure. All methods gave the same order of retardation, with benzene, the most soluble, showing the least retardation, and xylene, the least soluble, showing the highest degree of retardation. In addition, all methods gave very similar results for a particular compound, providing no significant basis for a preference of methods based on accuracy. The results suggest that all the compounds are



relatively mobile in the sand material of the Borden aquifer. Considering the very low organic carbon content and low clay content of the Borden aquifer material, these results are not unexpected. The column results indicated that the retardation process was affected by kinetic processes. The retardation factors were low which contributed to difficulties both in conducting the experiments and in the interpretation of the results. These uncertainties, and their relative significance should be more evident when the results of the field tracer test have been fully interpreted. In addition, tests conducted during the second year of the investigation, using soil materials with a range in values of organic carbon content, should provide further information concerning the applicability of the various test procedures.

Natural-Gradient Injection Experiment

Planning and preparation for the natural gradient field test in the unconfined sand aquifer of CFB Borden was initiated in May, 1984. Cores of aquifer material were obtained and additional piezometers installed. In the laboratory, appropriate techniques were developed to rapidly determine benzene, toluene, and xylene (BTX) concentrations in the ppb range using solvent extraction and gas chromatography. These procedures are a new development which allow the processing of a large number of samples within a relatively short period of time, and yield accurate results. All equipment to be used at the injection site was first assembled, tested, and modified in the laboratory to minimize problems in the field.

The field injection procedure consisted of i) the preparation of a spike solution containing dissolved BTX and chloride, ii) mixing and diluting the spike solution with groundwater from a storage reservoir, and iii) metering the dilute solution through a single injection well. The system was assembled in the field in early August, 1984 and the injection commenced following a brief trial run. A total of 1800 litres of dilute BTX solution was injected over a period of 21 hours.

Since the injection five 'snapshot' sampling sessions have been completed and over 3200 samples have been analysed for BTX and chloride. Because the sampling has encompassed the BTX plume both vertically and horizontally, the data provide a unique opportunity to examine the dissolved hydrocarbons in three dimensions. Results indicate that the slug is proceeding down-gradient and has assumed a shape which reflects the vertical heterogeneities of the aquifer material.

Analysis of the snapshot data to date has focused on defining the horizontal aspect of the plumes using vertically averaged concentrations of the chemical constituents. Two-dimensional contour plots have been produced which clearly illustrate that the BTX are being retarded relative to the chloride tracer. Evidence is also presented that mass losses of some of the constituents, (m-xylene in particular) have occurred.



Biodegradation Studies

Biodegradation studies have been delayed by the need to develop specific analytical techniques. A novel method using High Performance Liquid Chromatography (HPLC) has been developed, and several investigations are now underway.

Phase II Projects

There will be a continuation of all projects in Phase II. In the small scale sorption tests, retardation coefficients will be determined for BTX in a range of aquifer materials with varying organic carbon contents, using correlation equations, batch isotherm procedures, and laboratory columns. In addition, experiments will be performed to identify the apparent loss of mass observed in laboratory column experiments in Phase I. The natural gradient field test will continue with further monitoring in the spring. Contaminant concentrations will also be mathematically modelled to assess the extent and predictability of advection dispersion, sorption, and transformation processes on BTX migration. In the biodegradation studies, laboratory batch tests will be performed to establish biodegradation processes and rates, and further assessments of biological activity from core samples will be conducted. As well, the effects of nutrient additions on BTX biodegradation in flask experiments will be studied.



CONTENTS

EXECUTIVE SUMMARY	11
Introduction	11
Small-Scale Retardation Tests	11
Natural-Gradient Injection Experiment	111
Biodegradation Studies	iv
Phase II Projects	iv
 INTRODUCTION	1
Objectives	2
 SMALL-SCALE RETARDATION TESTS	4
Introduction	4
Background	4
Experimental Procedures	8
Materials	8
Batch procedures	10
Laboratory Column Procedures	10
In-situ column procedures	10
Analytical Procedures	10
Results and Discussion	11
Calculated Retardation Factors	11
Batch Experiments	13
Laboratory Column Experiments	16
Field Column Experiments	19
Summary of Results	22
 THE NATURAL GRADIENT INJECTION EXPERIMENT	25
Introduction	25
The Borden Site	25
Existing Monitoring Network	26
Injection Well Design	28
Piezometer and Well Construction and Installation	29
Injection Composition	33
Injection System	34
The Field Injection	36
Sampling Procedures	37
Laboratory Procedures	39
Data Analysis and Preliminary Results	40
 BIODEGRADATION STUDIES	48
 Phase-II Projects	49
Introduction	49
Evaluation of Methods for Measuring Retardation	50
Natural-Gradient Field Test	50



Biodegradation and Remediation Using Enhanced Biodegradation	51
Glossary of Contaminant Hydrogeology Terms	53
REFERENCES	54
Appendix A: Batch procedures	56
Appendix B: Laboratory Column Procedures	58
Appendix C: In-situ column procedures	62
Appendix D: Hexane Micro-Extraction for the Determination of Purgeable Aromatics in Groundwater	64
Introduction	64
Experimental	65
Results and Discussion	66
Conclusions	66
Acknowledgements	67
References	67

FIGURES

2.1	Isotherms for benzene and toluene.	14
2.2	Laboratory column results, $v = 22$ cm/day.	17
2.3	Laboratory column results, $v = 150$ cm/day.	18
2.4	Field column results, $v = 150$ cm/day	20
2.5	Field column results, $v = 340$ cm/day	21
3.1	A typical multilevel piezometer installation	27
3.2	Locations of multilevel piezometers	31
3.3	Injection well and piezometer installations.	32
3.4	Schematic of the BTX injection system.	35
3.5	Chloride contour plan 53 days after injection.	42



3.6	Benzene contour plan 53 days after injection.	43
3.7	Toluene contour plan 53 days after injection.	44
3.8	P-xylene contour plan 53 days after injection.	45
3.9	M-xylene contour plan 53 days after injection.	46
3.10	O-xylene contour plan 53 days after injection.	47
B.1	Schematic of the column used in the laboratory experiments.	59
B.2	Schematic of the laboratory column apparatus.	60
C.1	Schematic of the field column device.	63
D.1	Typical sample chromatogram. Conditions described in text.	68

TABLES

2.1	Physical Characteristics of the Borden Aquifer Material.	9
2.2	Hydrophobicity Parameters at 25°C and Calculated K_d and R for Experimental Compounds	12
2.3	Distribution Coefficients Measured with Batch Equilibration Technique at 10°C	15
2.4	Comparison of retardation factor (R) values.	23
3.1	Core Lengths and Locations from the Borden Site	30
3.2	Preliminary Injection Data	36
3.3	Preliminary Calculations of Mass of Chemicals Injected	37
3.4	Snapshot Sampling Information	40
D.1	Method Detection Limit	69
D.2	Accuracy and Precision at Typical Sample Concentrations	70
D.3	Analysis of USEPA Quality Control Sample WP 879 #1	70

INTRODUCTION

Dissolved organic compounds from spilled or leaked petroleum products represent a hazard to groundwater quality in permeable formations because many of them are quite soluble and, in some circumstances, quite mobile. The influence of volatilization and the processes controlling dissolution of water-soluble components of the resultant organic liquid phase will not be addressed in this study, although they are important processes controlling the resultant groundwater contamination. Groundwater transport migration processes include advection and dispersion while processes such as sorption and chemical or microbial transformation may limit the extent of transport. In any particular situation it is not possible with existing knowledge to reliably predict the influence of all these factors on the transport of soluble, petroleum-derived hydrocarbons. This causes large uncertainties in the prediction of the environmental impact of petroleum products on groundwater. It makes the design, implementation and evaluation of remedial actions taken to minimize the spread of soluble organics equally uncertain.

The goal of this three-year research program initiated in 1984 is to develop an improved understanding of the influence of advection, dispersion, sorption and transformation upon the transport, in groundwater, of selected organic compounds that commonly enter groundwater in dissolved form from spilled or leaked petroleum products. This will aid the petroleum industry and its consultants in the design and use of groundwater monitoring networks, in the assessment of the likely transport and fate of dissolved organic contaminants and in the evaluation of options for remedial actions required to limit or reduce the spread of such contaminants. Direct benefits will include:

1. evaluation of natural processes that control contaminant movement
2. evaluation of means to assess sorption and biodegradation-processes that could retard the movement of contaminants
3. provision of an in situ tester for field measurement of sorption
4. evaluation of in situ remedial techniques using microbial degradation
5. identification of critical parameters which must be determined to properly deal with groundwater contamination by BTX (benzene, toluene, xylene)

This research is concentrating upon the organic contaminants: benzene, toluene, and xylenes (meta-, ortho- and para-). These are common constituents of petroleum products, quite soluble in groundwater and of considerable environmental concern as reflected by the interest of regulatory agencies to limit their levels to the low ppb range in drinking waters.

Of the many types of hydrogeological systems that could be impacted by these contaminants, the field component of this research program has focused upon permeable surficial sand deposits which form unconfined sand aquifers. These are common aquifers in many urban areas, and because of their near-surface and permeable nature, represent a hydrogeological environment susceptible to rapid and extensive contamination by petroleum products. In addition, the scientific framework for contaminant transport studies is probably best developed in such a porous medium. The results of this study will be generalized to other media in a later phase.

1.1 Objectives

The objectives of the research program are five-fold.

1. To assess the accuracy and applicability of the conventional methods and two newly-developed methods for determining the adsorptive retardation of the selected organic compounds during transport by groundwater in sand aquifers.
2. To develop and assess practical methods for determining the extent to which biodegradation will attenuate the selected organic compounds as transport by advection and dispersion occur in sand aquifers.
3. To test and evaluate the balanced nutrient method of remedial action for groundwater zones contaminated with the selected organic compounds and to evaluate the role of dispersion in this method.
4. To make use of the information obtained in the three objectives mentioned above in evaluating other options for remedial action that have been described in the literature or are currently being developed.
5. To broaden the results of this study to consider migration and possible remedial actions pertinent to other hydrogeological environments.

The specific tasks undertaken in Phase I were:

1. To perform calculations, laboratory experiments, and field experiments with an in situ tester to define the adsorptive characteristics of the Borden sand for benzene, toluene, xylene(s).
2. To design and initiate a natural gradient field test at the Borden site to evaluate adsorptive and biodegradation aspects of retardation and to evaluate the influence of advection and dispersion on the transport of the compounds. This experiment will not be completed until 1985/86. The results will be used to assess the suitability of laboratory tests as predictive tools.
3. To critically compare the results of the various laboratory and field methods for assessing adsorptive retardation of these organic compounds.

4. To test, in the laboratory, the biodegradability of these organic compounds under conditions approximating those at the Borden site. To initiate testing of possible balanced nutrient additions to promote biodegradation of these compounds in preparation for field testing in 1985/86.

This PACE-sponsored research commenced in April, 1984. This report summarizes the progress made in Phase I until the end of 1984.

The progress is presented in three sections. The first deals with the laboratory and field study of the sorptive characteristics of the organic compounds. The second presents the natural gradient injection experiment and the third describes the preliminary, microbiological work. The results of the natural gradient experiment are just being interpreted and so the important comparison of lab predictions with actual field results cannot be made as yet. The biodegradation studies have also been delayed because of a need to develop specific analytical techniques. Overall, however, progress in Phase I has been excellent and plans for Phase II have been prepared and are presented in a later section of this report.

SMALL-SCALE RETARDATION TESTS

2.1 Introduction

Moderate- to large-scale tracer tests, such as the natural-gradient tracer experiment described in Ch. 3 of this report, provide the best means of identifying and quantifying the factors that control the migration of a particular contaminant under natural hydrogeologic conditions. Though such tests are valuable for identifying and studying processes, because of the time required and the cost, they are impractical for assessing the potential for contamination at specific sites of contamination. As an alternative, there are a variety of small-scale test procedures that can be used to evaluate the potential for geochemical retardation of contaminants at specific sites. Combining the results of these tests with the hydrogeologic characteristics of the site should, in principal, provide a means of estimating the migration rate of the contaminant at the site. Generally the test procedures are relatively inexpensive and can be executed within a short period of time. If such procedures do in fact provide retardation values that are representative of field conditions, then they provide a very practical solution to the problem of predicting the future migration of existing zones of contamination.

Three small-scale methods for determining retardation coefficients for benzene, toluene and xylene were investigated. These included batch distribution coefficient measurements, laboratory column experiments and an in situ field column procedure. A fourth procedure involved the use of literature-derived regression equations to calculate sorption coefficients from measurements of the organic carbon content of the aquifer material and the hydrophobicity of the compounds. The objective of this portion of the study was to evaluate the accuracy of the various procedures through comparisons with the retardation observed in the large-scale injection experiment, to identify particular limitations of the various procedures when applied to BTX, and ultimately, to recommend procedures that could be applicable for evaluating retardation at sites of contamination.

2.2 Background

The transport of dissolved chemical species through water-saturated porous media is influenced by a wide variety of chemical and physical processes including advection, dispersion, chemical precipitation and dissolution, formation of complexes in the aqueous phase, chemical and biochemical degradation, and sorption. The basic equations describing the transport of reactive solutes have been presented by several investigators (e.g. Bear, 1972 and Freeze and Cherry, 1979). If sorption is the only chemical reaction consid-

ered, the equation used to describe the movement of solutes in saturated, homogeneous porous media under conditions of one-dimensional steady flow is (Lapidus and Amundson, 1952)

$$\frac{\partial C_i}{\partial t} = D \frac{\partial^2 C_i}{\partial x^2} - V \frac{\partial C_i}{\partial x} + \frac{\rho}{n} \frac{\partial Q_i}{\partial t} \quad (1)$$

where:

C_i is the aqueous-phase concentration of solute i
(M/L³)

Q_i is the sorbed-phase concentration of
solute i (M/M sediment)

n is the porosity of the porous medium

ρ is the bulk density (M/L³)

D is the hydrodynamic dispersion coefficient in the
x-direction (L²/T)

V is the mean porewater velocity in the x-direction (L/T)

x is distance (L) and

t is time (T).

For ideal plug flow, without dispersion, a sharp concentration front is maintained between two miscible fluids. Dispersion acts to spread the sharp front resulting in a smeared concentration profile moving at the mean porewater velocity (V). The sorption of a contaminant causes it to migrate at a velocity less than the mean porewater velocity, and, coupled with dispersion, results in a further flattening and spreading of the concentration profile.

The solution of Eq. (1) requires an expression relating the sorbed-phase concentration, Q_i , to the aqueous-phase concentration C_i . In a general form the relationship between Q_i and C_i may be written as

$$Q_i = Q_i(C_1, C_2, \dots, C_n, s, t) \quad (2)$$

where s is a space variable. Equation (2) implies that the amount of solute i which is sorbed is in general a function of all the solutes present, the position s and time t .

If it is assumed that the adsorption-desorption process is completely reversible, a linear relationship exists between Q_i and C_i and the system is at local chemical equilibrium, and, if it is further assumed that the sorption process is independent of the behaviour of other solutes and is spatially uniform, the problem is simplified considerably. Based on the above conceptualization, the solute transport model can be restated as follows:

$$\frac{\partial C_i}{\partial t} = D' \frac{\partial^2 C_i}{\partial x^2} - V' \frac{\partial C_i}{\partial x} \quad (3)$$

where $D'=D/R$ is the dispersion coefficient for the reactive solute, $V'=V/R$ is the mean velocity of the reactive solute and R is the retardation factor defined as:

$$R_i = 1 + (\rho/n) K_d \quad (4)$$

The variable, K_d , is referred to as the distribution coefficient. The distribution coefficient relates the amount of a chemical species sorbed on the solid phase to the amount of the species remaining in the solution phase by:

$$Q_i = K_d C_i \quad (5)$$

where Q_i and C_i are as previously defined.

In order for Eq. 3 to be applicable, several conditions must be met. In particular, it is required that local equilibrium be achieved along the flow path, that the sorption reactions can be described by a linear relationship and that the reactions are independent of changes in the concentrations of other chemical species. There is a growing body of evidence in the literature, including the results of both laboratory and field experiments, indicating that the above assumptions are frequently not satisfied and thus that Eq. (3) does not adequately account for the actual chemical changes along the flow path. The inability of this model to describe the observed behavior has been attributed to mechanisms such as kinetic limitations due to mass transport to and from sorption sites or relatively slow sorption-desorption processes, hysteresis between adsorption-desorption processes, and a variable distribution coefficient in both space and time due either to major ion composition changes along the flow path or spatial variability in the porous materials. Ionic species are particularly sensitive to changes in ion composition and small changes in ionic strength, while uncharged or non-polar species are relatively insensitive to these changes. The species investigated in this study were all nonionic and at low concentrations, and it was expected that the

sorption process would be relatively independent of changes in the major ion composition or small changes in ionic strength of the solutions.

For many sediment-water systems, the distribution coefficients for many nonionic compounds have been observed to increase in proportion to the solid phase organic matter content of the matrix (Chiou et al., 1979; Schwarzenbach and Westall, 1981; Karickhoff, 1981 and 1984). Generally, from the sorption of a large number of hydrophobic compounds it has been found that K_d can be referenced to the organic carbon content (f_{oc}) of the sediments. The resulting organic carbon partitioning coefficient, K_{oc} , was found to be relatively constant for a wide range of sediments and soils (Karickhoff, 1981; Chiou et al., 1979) and as a result was found to be related to the distribution coefficient by the expression:

$$K_d = f_{oc}(K_{oc}) \quad (6)$$

Many methods have been proposed to estimate K_{oc} and these have recently been reviewed by Karickhoff (1984). The most commonly used methods are based on semi-empirical correlations with the aqueous solubility, S , or the octanol-water partitioning coefficient, K_{ow} . Typically linear regression equations of the following form are used

$$\log K_{oc} = A \log K_{ow} + B \quad (7)$$

$$\log K_{oc} = -C \log S + D \quad (8)$$

in which A , B , C , and D are regression-fitted parameters. In general, the more nonpolar a molecule, the lower its water solubility and the larger its K_{oc} and K_{ow} values. Equations (7) and (8) have been observed to successfully predict the sorption of a large number of hydrophobic solutes onto a wide range of materials, particularly for sorbents with high organic carbon contents, and at low concentrations of the sorbate. The predictions have been less successful for compounds having high polarity and for sorbents with low organic carbon contents, especially with a coincident high clay content. A recent review by Mingelgrin and Gerstl (1983) outlines many of the limitations of the above regression models.

2.3 Experimental Procedures

2.3.1 Materials

The sorbent material used in the laboratory experiments was obtained from the site of the natural-gradient injection experiment and the field column experiments at Borden, Ontario. Characteristics of the sand sample are given in table 2.1. A petrographic analysis of a second sample of material obtained in the vicinity of the field experiments showed that the sediment was predominantly quartz (40-50%), but also contained appreciable amounts of amphibole (15-20% hornblende), feldspars (10-15% plagioclase and 5-10% orthoclase) and carbonates (8-10%), with biotite, garnet, magnetite and small amounts of chlorite present as accessory minerals (Dance, 1983).

The organic solutes used in this study included benzene, toluene, o-xylene, m-xylene and p-xylene and all were obtained as reagent grade chemicals of greater than 99% purity. In addition, two of the compounds, benzene and toluene were obtained as carbon-14 radio-labelled materials. Stock solutions were made by spiking simulated groundwater solution with a standard mixture of one or more of the organic solutes in methanol. In all cases, less than 200 μ l of the spiked methanol was added per litre of water.

To prevent dissolution of the calcium carbonate in the sorbent material during the laboratory studies, it was desirable to use water that was in equilibrium with carbonate at atmospheric P_{CO_2} . It was also desirable to use water which was free of other hydrocarbons. In preparing the simulated groundwater, double-deionized water was pumped through activated charcoal, irradiated with ultraviolet light for 30 min., and purged with filtered N_2 gas for 2-4 hr to remove organic compounds present in the water.

Calcium carbonate was added to the water at a concentration that would occur in pure water in equilibrium with calcite at atmospheric P_{CO_2} . This solution was purged for several hours with pure CO_2 gas to rapidly dissolve the $CaCO_3$. The solution was then purged with purified gas at atmospheric P_{CO_2} until the solution pH was constant. This procedure resulted in a solution with an ionic strength slightly lower than the groundwater at the field site, and a pH of approximately 8.3. The solution prepared for the column experiments contained only trace amounts of oxygen to minimize the effects of biodegradation during the experiments. Oxygen was allowed to enter the solutions used in the batch experiments.

Table 2.1: Physical Characteristics of the Borden Aquifer Material.

Particle size *	%
sand (20 to 50 microns)	96.00
silt (2 to 20 microns)	2.00
clay	2.00
 Solid-phase organic carbon	 0.02

* U.S. Department of agriculture size classification

2.3.2 Batch procedures

In general, batch tests involve the addition of a given volume of solution containing the tracer (contaminant) of interest to a given mass of soil. After sufficient time has elapsed for chemical equilibrium to be reached, the concentration of the tracer in the liquid and solid phases is determined, providing a single point on the adsorption isotherm. By varying the initial concentration in the solution phase, the isotherm can be established over the concentration range of interest. Provided the isotherm is linear and passes through the origin, its slope is the partitioning parameter (K_d) required by the transport model (equation 3). Details of the procedure used in this study are given in Appendix A.

2.3.3 Laboratory Column Procedures

Column experiments are dynamic in nature and thus the results show the effect of geochemical retardation processes superimposed on the effects of advection and dispersion. They are therefore more representative of field conditions than batch tests, and have the potential to reveal the effects of kinetic adsorption processes and irreversible adsorption processes. Column experiments are generally conducted by displacing tracer-free solution from a column with solution containing the tracer. The retardation process is then evaluated from the graph of effluent concentration versus time. The analysis of the effluent curve is frequently facilitated by comparing reactive and non-reactive effluent curves.

Column experiments are frequently conducted either as continuous input experiments, where the tracer solution is injected over a long period of time, or as pulse experiments, where the tracer is injected over a short time interval. Pulse experiments were used in this study, and effluent curves were measured for a non-reactive tracer (chloride) as well as for the reactive tracers, benzene, toluene and xylene. Details of the experimental procedures are given in Appendix B.

2.3.4 In-situ column procedures

The principles of the in-situ column procedure are identical to those given above for the laboratory column. However, the tests are conducted in the field, and in a manner that greatly minimizes possible effects of geochemical disturbance. Though the device and field procedures are still in the developmental stage, the results to this point suggest that it may be a very practical means of determining the in-situ retardation characteristics of contaminants at sites of contamination. Details of the apparatus and procedures are given in Appendix C.

2.3.5 Analytical Procedures

The unlabelled compounds were analysed using a liquid-liquid extraction procedure followed by flame-ionization detection gas chromatography. Standards were prepared following the procedure described by Glaze et al. (1983),

however, other aspects of this procedure were modified. The procedure provided in Appendix D describes these modifications.

For samples containing labeled compounds, the activity of carbon-14 was determined on a MARK III Liquid Scintillation Spectrometer with Aquasol 2 cocktail (New England Nuclear, Boston, MA). Counting data were corrected for background, quenching and dilution factors. The precision of the method was generally better than $\pm 3\%$ and the detection limit was approximately 50 ng/L for each of the organic compounds.

2.4 Results and Discussion

2.4.1 Calculated Retardation Factors

The compounds that were investigated are listed in Table 2.2 with their aqueous solubilities, S , and octanol/water partitioning coefficients, K_{ow} .

Retardation factors (R) for the five compounds were calculated from the solubility and K_{ow} values using the procedure outlined previously. That is, the organic carbon partitioning coefficients (K_{oc}) were calculated from the regression equations (equations 7 and 8), and the distribution coefficients (K_d) were determined using the K_{oc} values and the organic carbon content of the aquifer material, as expressed by Eq. (6). Equation (4) was then used to determine the retardation factor (R). As noted earlier, organic-carbon partitioning coefficients have been correlated to S and K_{ow} for a wide variety of hydrophobic compounds and sediments and soils. The regression coefficients from the resulting equations have been found to vary slightly, depending on the compounds and the sediments used in the studies. The regression coefficients reported by Schwarzenbach and Westall (1981) ($A = 0.72$, $B = 0.49$ for Eq. 7) and Chiou et al. (1979) ($C = 0.56$, $D = 4.3$ for Eq. 8) were used in this study.

The determination of K_d from K_{oc} requires a knowledge of the organic carbon content of the sorbent. The organic carbon content of the Borden aquifer material was determined to be approximately 0.02% (Table 2.1). The equations relating K_{oc} to S or K_{ow} have been observed to provide reliable estimates of partitioning coefficients for sorbents with greater than 0.1% organic carbon. Below this concentration, the estimates are considered less reliable. Despite these potential limitations, calculations have been provided for Borden sand to assess the applicability of the estimation procedure for sorbents characterized by low amounts of solid-phase organic carbon.

Equation 4, used to calculate the retardation factors, requires values for the bulk density and porosity of the porous medium. A value of 1.7 g/cm^3 was used for the bulk density and 0.38 for the porosity. These values are estimates of the bulk density and porosity based on measured values at a nearby site as reported in Sudicky et al. (1981). Relative to the uncertainty in the estimated K_d values, small errors in the bulk density and porosity determinations are insignificant in the overall R determinations. The calculated retardation factors are included in Table 2.2. These will be compared with the measured values in a later discussion.

Table 2.2: Hydrophobicity Parameters at 25°C and Calculated K_d and R for Experimental Compounds

Solute	Benzene	Toluene	o-xylene	p-xylene	m-xylene
Solubility, S (ppm) (1)	1740	554	167	157	134
Octanol-water partitioning coefficient, K_{ow} (2)	140	380	880	1410	1580
K_d (cm^3/g), calculated from solubility (3)	0.01	0.03	0.06	0.06	0.07
from K_{ow} (4)	0.02	0.04	0.08	0.11	0.12
R, calculated from solubility (3)	1.1	1.1	1.3	1.3	1.3
from K_{ow} (4)	1.1	1.2	1.4	1.5	1.6

- (1) averaged values from Kebe et al., 1974
- (2) averaged values from Hansch and Leo, 1979
- (3) Chiou et al., 1979
- (4) Schwarzenbach and Westall, 1981

2.4.2 Batch Experiments

The isotherms measured using carbon-14 labelled benzene and toluene are shown in Figure 2.4. The slopes (K_d) and intercepts of the isotherms were calculated by applying the least-squares method to the equilibrium solution data. The results of the analysis together with the 95% confidence intervals for the slope are provided in Table 2.3.

For the concentration range studied, and within the error of the measurements, reasonable linearity of the isotherm was observed. In sufficiently dilute systems, isotherm linearity is common for many hydrophobic compounds in natural sediments. Based on thermodynamic considerations Karickhoff (1984) suggests that if the equilibrium aqueous phase concentration of a hydrophobic solute is less than one half of its aqueous solubility and below 10^{-5} M, it can be expected that sorption isotherms measured in natural systems will be linear. The range in concentration covered in the batch experiments of this study were all below one half of the compounds solubility and less than or approximately equal to 10^{-5} M. Thus, the linearity observed is consistent with the theoretical considerations of Karickhoff (1984).

Table 2.3 also includes K_d values from preliminary experiments conducted without labelled compounds. As noted previously, these results had a high degree of scatter. The sorption experiments were conducted at only one initial concentration (approximately 0.5 g/m^3), and all five solutes were present in the equilibrating solutions.

The distribution coefficients measured with the unlabelled material were observed to be inversely related to their solubilities at 25°C and directly related to their K_{ow} values at 25°C . The distribution coefficients obtained from the experiments conducted with the labelled compounds do not, however, vary inversely with the S and directly with the K_{ow} values. In addition, the magnitude of the K_d values obtained from the experiments with the unlabelled compound were also lower than the values obtained from the isotherms obtained using the labelled compounds. The reasons for this discrepancy are unclear at present.

Retardation factors were calculated from the batch distribution coefficients using the relationship in Eq. (4). The bulk density and porosity values used in this equation were the same as those used to calculate the R values from the calculated K_d values. The results are included in Table 2.3.

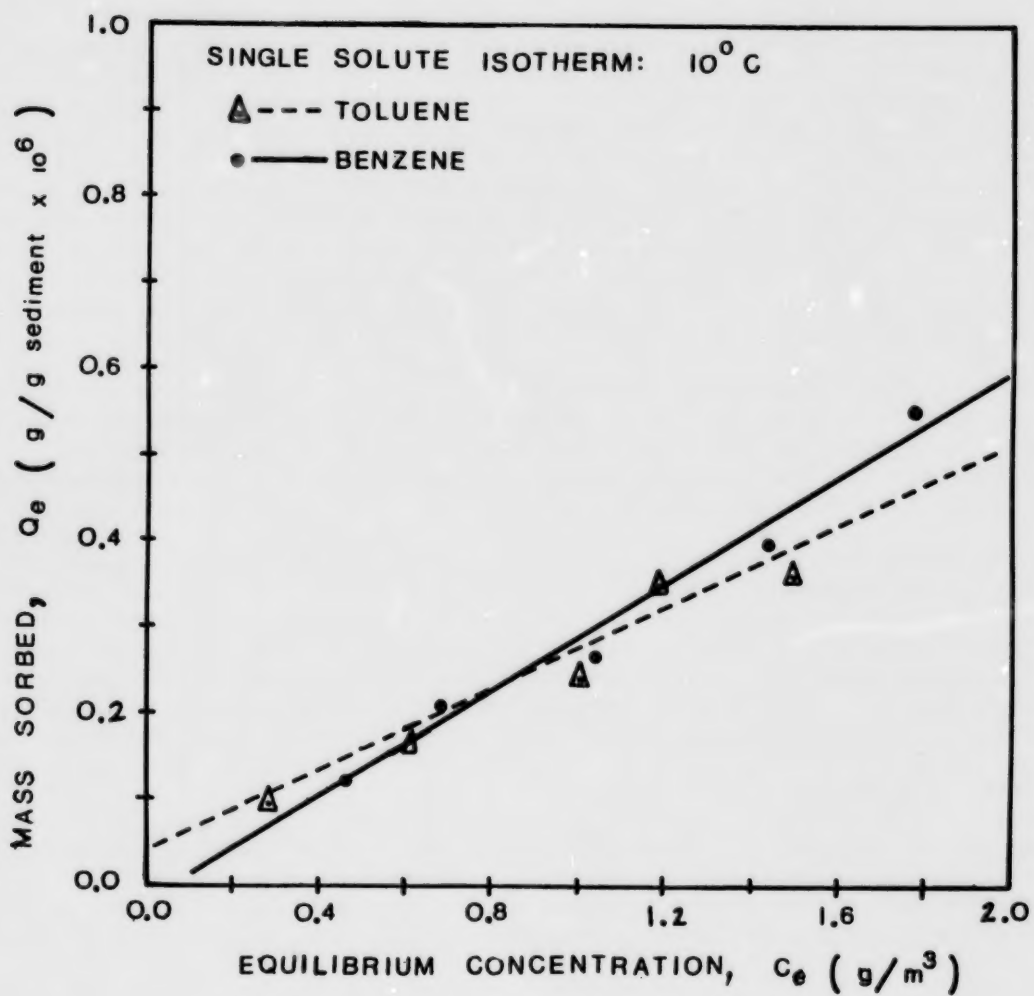


Figure 2.1: Isotherms for benzene and toluene.

Table 2.3: Distribution Coefficients Measured with Batch Equilibration Technique at 10°C

Isotherm results - single solute experiments

Compound	K_d ($\pm$ 95% CI) cm ³ /g	Intercept g/g sediment	r^2	Retardation factor (R)
Benzene	0.31 (0.03)	-0.02	0.995	2.4
Toluene	0.24 (0.04)	0.03	0.989	2.1

Point value results - mixed solute experiments*

Compound	K_d cm ³ /g	Retardation factor (R)
Benzene	0.05	1.2
Toluene	0.07	1.3
o-xylene	0.16	1.7
p-xylene	0.22	2.0
m-xylene	0.22	2.0

* preliminary results

2.4.3 Laboratory Column Experiments

Results obtained from the laboratory column studies are given in Figures 2.2 and 2.3. In these diagrams the normalized effluent concentration, C/C_0 , is plotted against dimensionless time (Pore Volumes). C is the concentration measured in the effluent, C_0 is the influent concentration and the number of pore volumes is the volume of effluent divided by the total volume of voids in the column. The effective pore volume was determined from the mean arrival time of a conservative tracer using the calculation method outlined below. A conservative tracer is a solute that does not interact with the solid phase or the pore water and is therefore transported at an average velocity equal to the velocity of the water. For each breakthrough curve the values of C/C_0 versus dimensionless time were connected with straight lines.

A progressive departure from one pore volume of the arrival time of the organic solutes was observed, indicating a progressive increase in the degree of retardation, with benzene showing the least retardation and p-xylene the greatest. The measured concentration profiles were observed to be highly asymmetrical relative to the concentration profiles measured for the conservative tracers. Although this asymmetry and tailing is inconsistent with the behaviour of the conservative tracer (not shown), it is a common characteristic of reactive solutes, with similar behaviour having been reported by Kay and Elrick (1967), Lindstrom and Boermsa (1974), van Genuchten et al. (1977), and others. This behaviour has been attributed to apparent nonequilibrium conditions in the porous medium (Kay and Elrick, 1967 and van Genuchten et al., 1977) and to spatial differences in sorption characteristics due to soil-pore geometry and distribution (Lindstrom and Boermsa, 1971.)

Values of the mean arrival time were calculated for each of the tracers in each of the experiments by determining the position of the centre of mass of the respective breakthrough curves. Retardation factors were then calculated by dividing the mean arrival time of the organic solute by the mean arrival time of the non-reactive tracer.

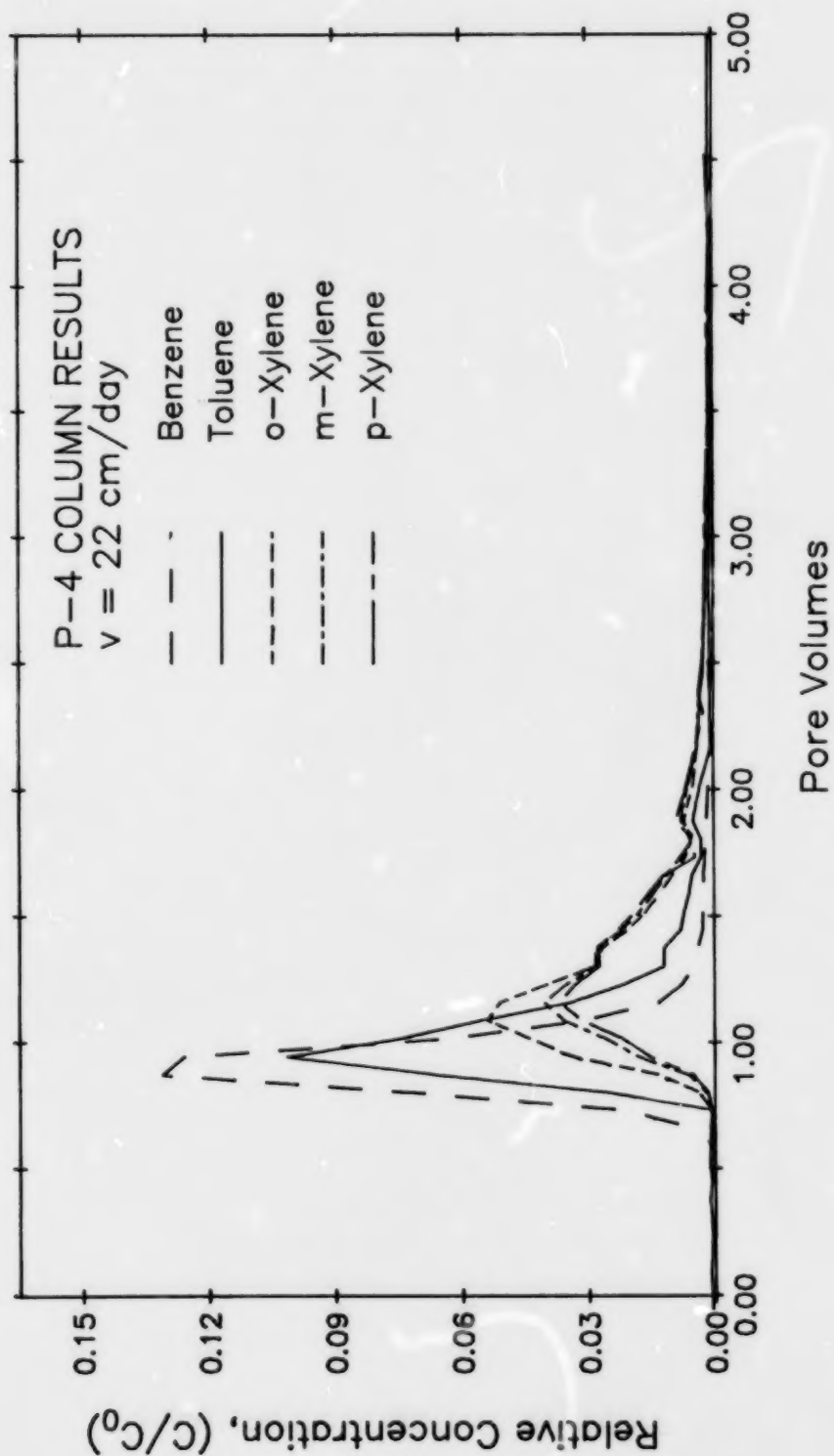


Figure 2.2: Laboratory column results, v = 22 cm/day.

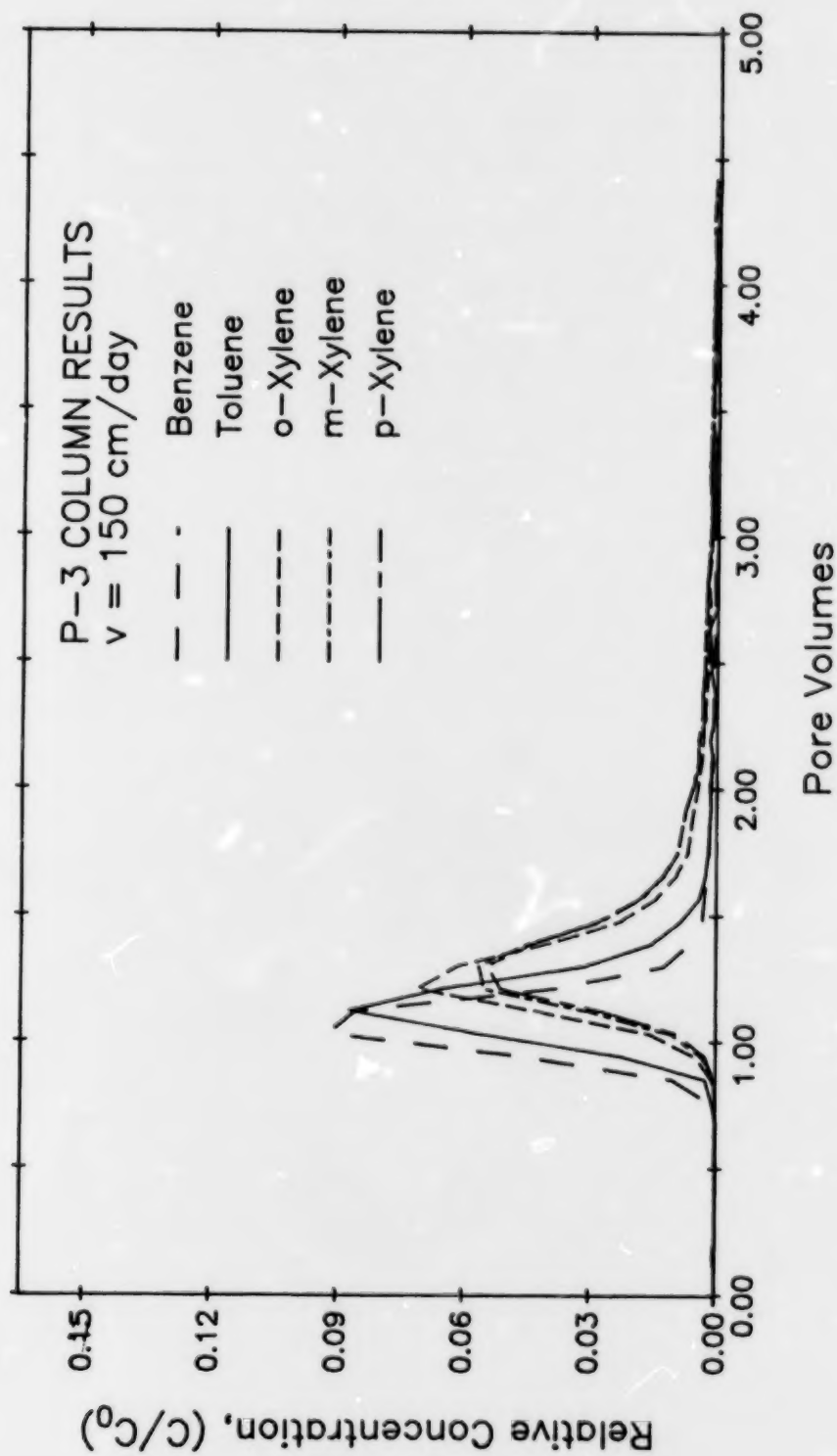


Figure 2.3: Laboratory column results, v = 150 cm/day.

2.4.4 Field Column Experiments

Miscible displacement column experiments were conducted in the field with a column device that was installed approximately one meter below the water table. Results of the experiments are given in Figures 2.4 and 2.5. In these diagrams, the normalized effluent concentrations are plotted as a function of dimensionless time in the same manner as in Figures 2.2 and 2.3.

The transport of the organic solutes observed in the field experiments was consistent with the transport observed in the laboratory. All five compounds were retarded with respect to the conservative tracer and the order of retardation was the same as observed in the laboratory experiments. At the lower velocity of 190 cm/day, the retardation was somewhat greater than for the higher velocity.

The R values were determined from the field breakthrough curves using the same one-dimensional approach that was used to analyze the results of the laboratory column experiments. Because the solutes were injected as a line source in the field column experiments, the assumption of one-dimensional transport may not be satisfied. Although this could lead to errors in the calculated R values, because R is determined by comparing the effluent history of the reactive solute with the non-reactive solute, the error is expected to be very small.

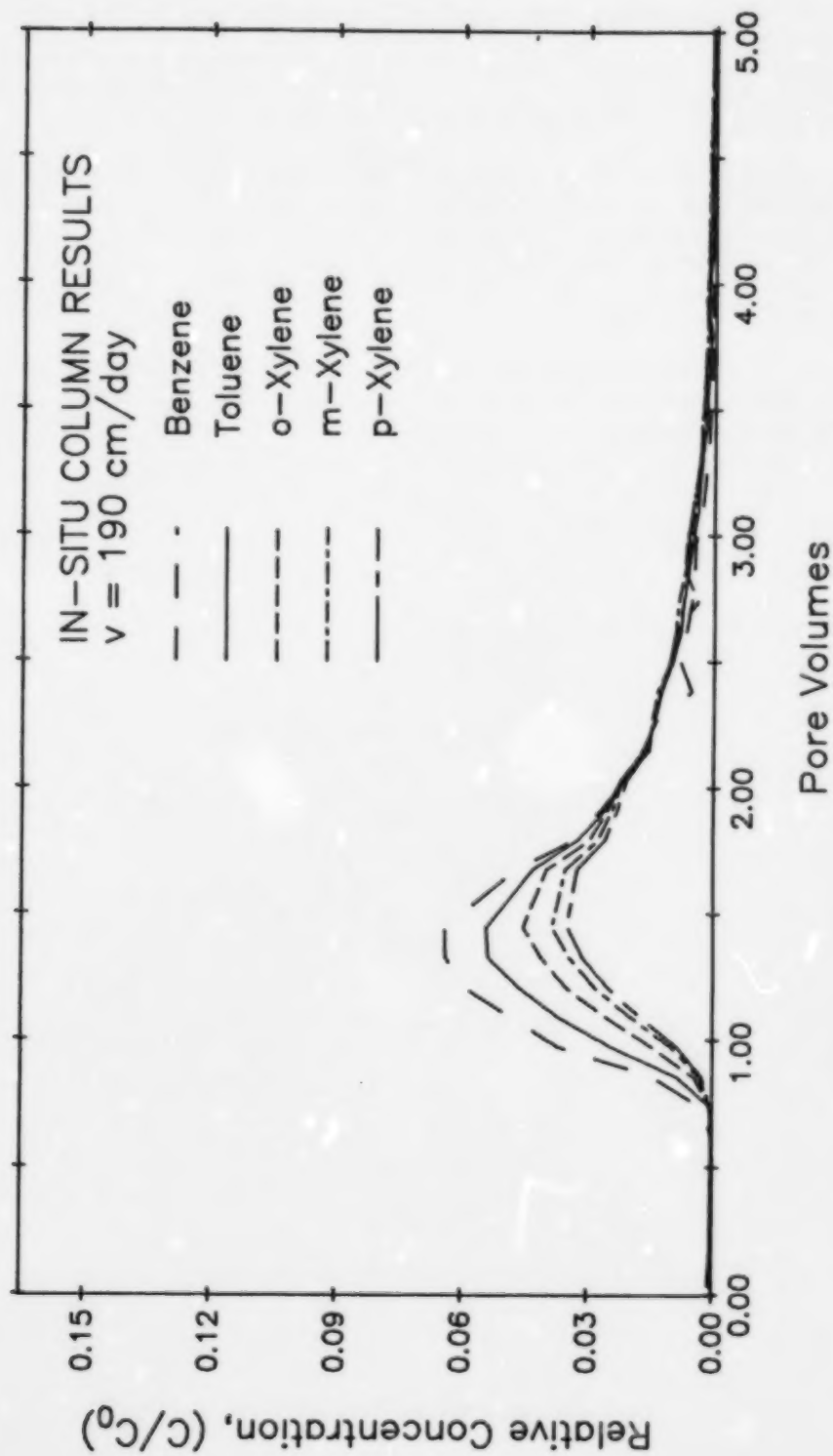


Figure 2.4: Field column results, $v = 150 \text{ cm/day}$

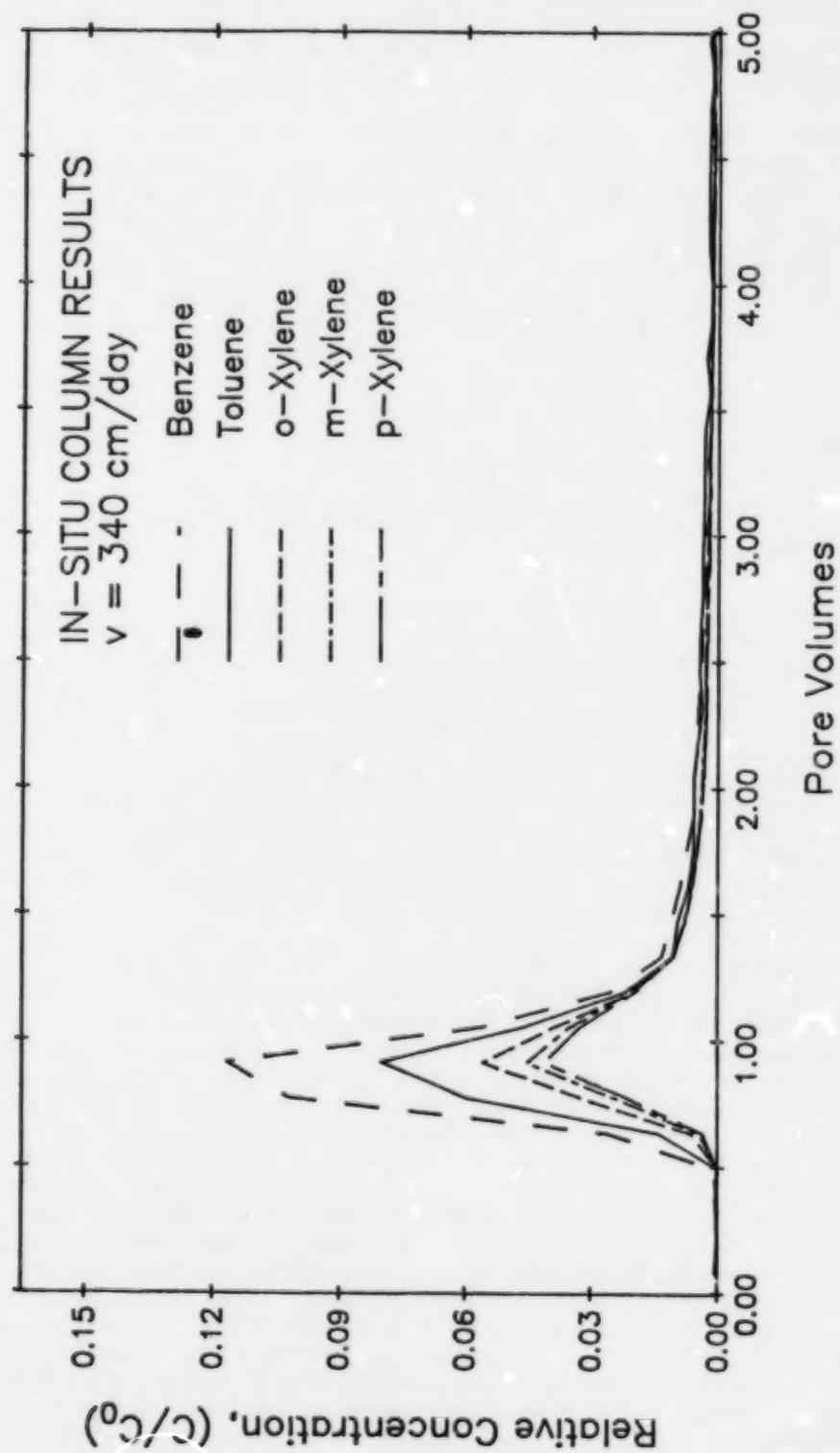


Figure 2.5: Field column results, $v = 340 \text{ cm/day}$

2.5 Summary of Results

The results of the batch equilibration experiments, laboratory and field column experiments, and the calculation technique are summarized in Table 2.4.

From Table 2.4 it can be seen that the rank-order of R values determined with each of the methods was the same, with benzene being the least retarded and xylene the most retarded. Furthermore, by comparing tables 2.5 and 2.2, it can be seen that the retardation is directly related to the hydrophobicity of the compounds. The R values obtained from all the methods were observed to be inversely related to the solubilities of the compounds and directly related to the K_{OW} values. The retardation factors measured in the miscible displacement column experiments were observed to vary with changes in the pore-water velocity, with the highest values generally obtained at the lowest velocities. This behaviour is consistent with a nonequilibrium reaction process. At high flow rates, nonequilibrium conditions may exist locally, resulting in a higher rate of advance than if local equilibrium prevails. Generally low flow rates are required to establish local equilibrium at all points along a flow path. It is expected that retardation factors measured at velocities similar to those occurring at the field site would provide the most realistic estimation of the retardation process.

Considering the uncertainty in the regression equations and the experimental uncertainties all methods gave remarkably similar retardation values. For benzene, the most mobile of the compounds considered, the range in retardation values indicate that it would move between 0.75 and 1.0 (unretarded) times the velocity of the groundwater. Similarly, xylene, the least mobile of the compounds, would move at between 0.5 and 0.7 times the groundwater velocity. Because of the very small range in the retardation values, there is no clear evidence to suggest that one method is more accurate than another. It appears that, to a first approximation, the calculation and the experimental methods provide retardation values that are in close agreement. A further evaluation of accuracy will be considered when the data from the natural gradient field test is fully analyzed.

The methods used in this study fall into two categories, static tests (calculated and batch) and dynamic tests (column). The static tests assume that a functional relationship exists between the solution and solid phase concentration according to the theory introduced in section 2.2. In addition, the calculation procedure provides a single K_d value, and to use this value in the transport equation, one must assume the existence of a linear sorption isotherm. In other words, the procedure provides no information concerning the nature of the sorption process or indeed, if reversible, sorption is the only geochemical mechanism affecting the transport process. In addition, the method is highly sensitive to uncertainties in the measured concentration of the organic carbon content of the sediment. Batch procedures provide a more direct measurement of the K_d and retardation factor, and provide a means of evaluating the linearity of the isotherm. They can also be used to evaluate the reversibility of the reaction, but are not an effective means of evaluating reaction kinetics. In addition, the results of such tests may be affected by geochemical alterations of the soil-water system from the in-situ conditions. Though batch tests are generally inexpensive and relatively quick to perform, for volatile trace organic constituents, there is substantial poten-

Table 2.4: Comparison of retardation factor (R) values.

	<u>Calculated</u>	<u>Batch**</u>	<u>Column</u>			
			<u>Field</u>		<u>Laboratory</u>	
			<u>340*</u>	<u>190*</u>	<u>150*</u>	<u>22*</u>
Benzene	1.1	1.2	1.3	1.4	1.1	1.0
Toluene	1.2	1.3	1.3	1.5	1.2	1.2
o-xylene	1.4	1.7	1.3	1.7	1.3	1.3
m-xylene	1.5	2.0	1.4	1.8	1.4	1.4
p-xylene	1.6	2.0	1.4	1.8	1.4	1.5

* Velocity in cm/day

** R values calculated from preliminary batch data using only one initial solution concentration

tial for experimental error, and a high degree of experience and expertise is required in order to obtain reliable results. Furthermore, at very low K_d values, such as those encountered in this study, there is generally a substantial degree of uncertainty in the results.

Dynamic procedures for evaluating retardation factors are generally more costly and time-consuming than the static procedures. However, in that they require an application of the transport model in order to arrive at the retardation coefficient, they have the potential to provide more information than the static methods. Deviations between measured and simulated results would suggest that retardation is not being entirely controlled by instantaneous, linear and reversible reactions. Depending upon the nature of the deviations, the results could show kinetic effects, non-linearity of the isotherm, irreversible uptake, or possibly the effects of biodegradation. In the present study, because of the experimental design, it was not possible to perform accurate mass balances on the respective breakthrough curves. Nevertheless, by considering the mass under the curves, there is the suggestion that some mass has been lost, possibly by irreversible uptake processes or slow desorption reactions. Such processes could be very important with respect to the prediction of the long-term migration characteristics of a contaminant plume, but would not generally be revealed by the static methods for evaluating the retardation coefficient. To determine if irreversible uptake or slow desorption processes are significant with respect to the migration of BTX, additional column experiments would need to be conducted, with great care being taken to obtain accurate measures of the mass balance. It should be noted that this is particularly difficult for volatile constituents at low concentrations.

Based on the similarity of the data in Table 2.4, and the fact that the process affecting the migration of BTX in hydrogeologic environments are not yet fully defined, there is no clear basis for recommending one procedure over another for determining retardation factors. This question should be further resolved by the experiments proposed for the 1985 study period.

THE NATURAL GRADIENT INJECTION EXPERIMENT

3.1 Introduction

The natural migration of dissolved hydrocarbons in groundwater has been studied, for the most part, at sites where accidental losses of petroleum or petroleum products have occurred. Often the volumes of the losses are unknown, and the hydrogeologic conditions at these sites are not well defined. As a result, our present understanding of the behaviour of many hydrocarbons in groundwater is relatively vague.

An alternative approach is to perform a controlled injection experiment where known volumes and masses of dissolved hydrocarbon constituents are injected into groundwater at a site where the hydrogeologic regime is known. By monitoring through time, changes in the size, shape and mass of the resulting plumes can be defined. This information can then be used to evaluate the migration patterns and specific attenuation mechanisms in the subsoil.

In the present investigation, the latter approach was used to evaluate the migration of benzene, toluene, and xylene compounds in groundwater under a natural gradient. The site, located at CFB Borden in southern Ontario, has been extensively studied in the past (Mackay et al., 1983a, MacFarlane et al., 1983).

Planning, preparation, and an evaluation of the injection design and laboratory methods commenced in May, 1984, and the injection was conducted on August 9 and 10 of that year. Since that time a series of five 'snapshots' of the plumes have been obtained by intensive sampling at three to four week intervals. This report describes the experimental design, and presents preliminary results obtained since the injection.

3.2 The Borden Site

The injection site is located in a sand pit a few hundred metres north of an abandoned landfill at CFB Borden in southern Ontario. The base of the pit is sparsely vegetated, relatively flat, and has a length and breadth of approximately 100 m. Previous and on-going investigations at the site have yielded a wealth of information regarding the subsurface structure and hydrogeologic properties of the Borden sand (Mackay et al. 1983a, MacFarlane et al., 1983). The sand is a fine to medium grained glacio-fluvial deposit which extends from surface to a depth of approximately 9 m, and is underlain by a relatively impervious clay. The sand exhibits small scale horizontal bedding with significant vertical hydraulic conductivity contrasts ranging as high as two orders of magnitude.

The groundwater regime is also well-defined at the Borden site. An unconfined aquifer is present in the sand, and the water table is at a depth of 0.5 m to 1.0 m. A leachate plume from the old landfill occupies the lower 6 m to 9 m of the aquifer, while the upper 5 m is unaffected. Groundwater in the upper zone is dilute, with a low specific conductance ($< 300 \mu\text{S/cm}$) and a neutral pH (7.4). It also has a significant dissolved oxygen content (1 to 7 mg/L). A previous injection experiment conducted jointly by Stanford University and the University of Waterloo (Mackay et al., 1983a) proved invaluable in the design and implementation of the present investigation. Results of that study had indicated that the groundwater velocity was constant at approximately 10.5 cm per day in a direction 27° east of North. At this velocity it was known that a plume could be tracked well beyond the proposed five to six month monitoring period for the present study.

3.3 Existing Monitoring Network

An added benefit of the Stanford-University of Waterloo study was that a dense monitoring network of multilevel piezometers was available. The network consisted of a grid of piezometers which extended from the original injection site to approximately 50 m down-gradient. The grid spacing was variable ranging from 1.0 m to 3.0 m. Each multilevel piezometer consisted of a series of 3.2 mm (1/8 in) O.D. teflon tubes spaced vertically at 20 cm intervals from depths of about 1.8 m to 4 m. A typical multilevel design is shown schematically in figure 3.1. The multilevels are easily sampled using a manifold system which allows the simultaneous collection of up to 14 samples from a single multilevel piezometer.

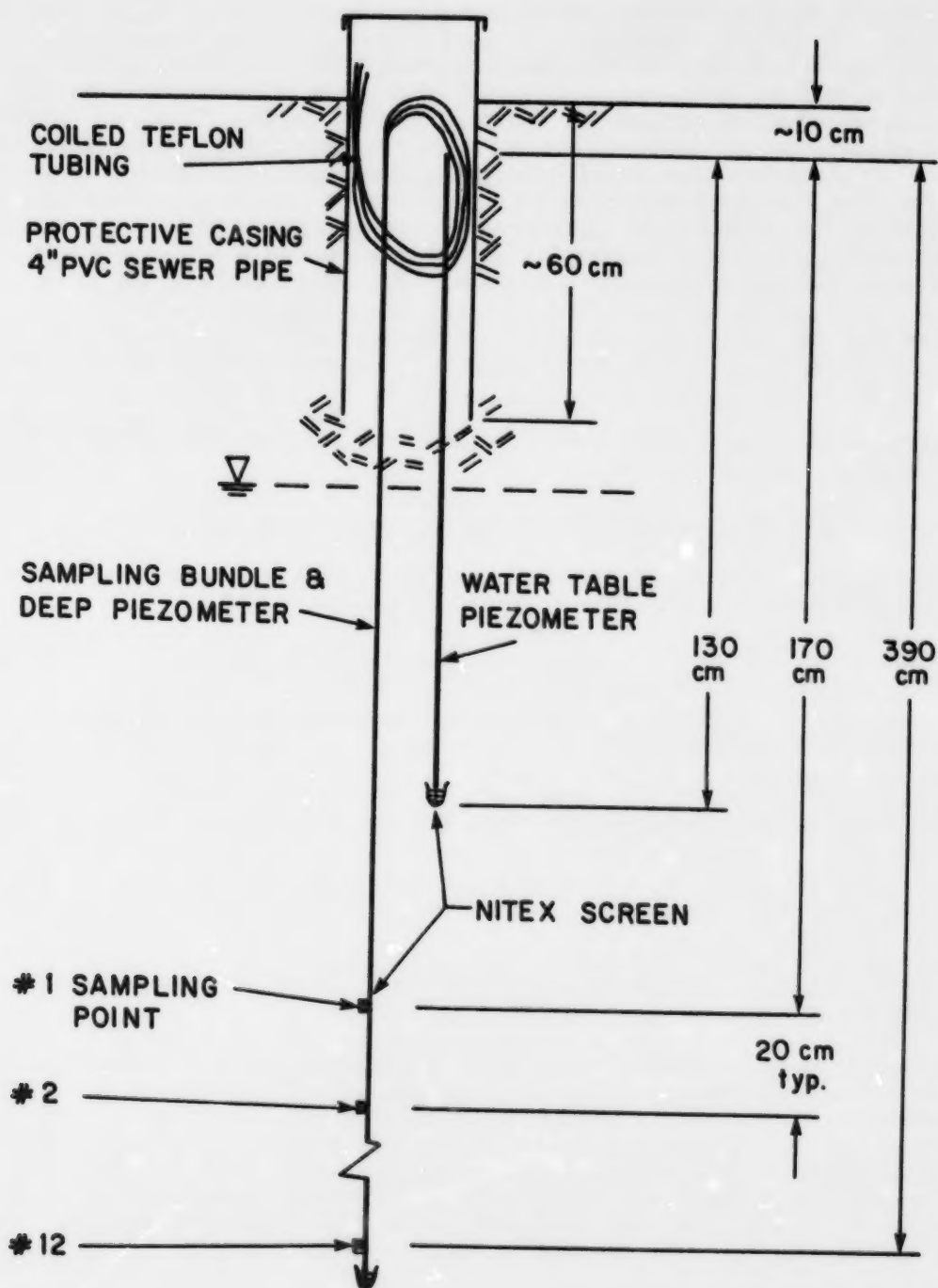


Figure 3.1: A typical multilevel piezometer installation. The multi-levels vary in the number of sampling points, and some may contain polyethylene rather than teflon tubing. In addition, the shallow water table piezometer may be omitted (adapted from Mackay et al., 1983a).

3.4 Injection Well Design

In the Stanford-University of Waterloo experiment, nine injection wells staggered in two rows were used to inject a 12 m^3 slug of dissolved compounds. Each well was screened vertically across 1.6 m of sand. This arrangement proved satisfactory although a relatively complex injection system was required, and some problems were incurred following the injection. Initial field data from sampling suggested that portions of the slug extended above the vertically monitored zone. Later data also suggested that the slug may not have entered the ground uniformly, but that a region of low concentration may have been produced between the two rows of injection wells.

An objective of the present study was to design a simplified system using a smaller slug size and a single injection well. The system could afford several advantages:

- * by screening the well over a shorter interval an excessive vertical rise of the slug would be avoided
- * a more uniform slug could be injected
- * a smaller slug size would be more compatible with existing manpower and equipment constraints during sampling and analysis
- * fewer samples combined with rapid analytical techniques would reduce the risk of chemical losses caused by excessive sample storage times.

Concerns with the proposed system were:

- * the slug size might be too small for the existing monitoring network to yield reliable data for mass balances and for determining the plume size and shape.
- * a significant portion of the slug might be removed by sampling over the monitoring period
- * injection through a single well could cause a significant perturbation to the natural groundwater flow regime

All concerns were carefully evaluated in relation to various proposed slug sizes, injection volumes, sampling frequencies, and other constraints. The first concern could be easily rectified by placing additional multilevels in the vicinity of the injection well and along the predicted flow path of the slug. Disturbance to the natural gradient was estimated using Hantush's correction method of Thiem-Dupuit's method for partially penetrated aquifers. Sample removal of the slug was evaluated using the constraint that no more than 10% of the slug could be removed in total over the duration of the study.

In the final design it was decided that a 2.0 m^3 slug would be injected through a single 31 mm (2 in) diameter well. The well would be screened over 0.5 m within the monitored zones. An optimum injection rate of 1.5 L/min or less was preferred to limit the extent of mounding at the well to about 10 cm or less. At this flow rate it would take approximately 22 hours to complete

the injection. It was hypothesized that the resulting plume would assume a spheroidal shape in the ground, having a vertical diameter at the well of about 1 m to 1.5 m, and a horizontal diameter of about 3 m.

To improve the density of the existing monitoring network, it was decided to place 17 additional multilevel piezometers at the site. This would increase the total number of potential sampling points in the network to well over 2000. The location of the injection well was chosen to maximize the use of the existing network, and locations for the new piezometers were chosen in the immediate vicinity of the injection well, and in the downgradient direction. It was proposed that most of the new piezometers have more monitoring points than the existing multilevels to span a greater thickness of sand. In addition, several shallow piezometers would be installed between the water table and the existing monitoring points. These precautions were necessary to ensure that the full size of the plume would be known, should the plume expand vertically to a greater extent than expected.

3.5 Piezometer and Well Construction and Installation

The additional piezometers and the injection well were constructed at the University of Waterloo prior to transport to the field for installation. The multilevels were patterned after the existing multilevel design shown in figure 3.1, although some modifications were made.

Polyethylene, rather than teflon tubing, was affixed to the PVC centre-stalks. While polyethylene is known to sorb organic compounds more readily than teflon, it was the material of choice because it was available and considerably less expensive. Short term laboratory tests had indicated that sorption of BTX by the polyethylene would not cause a significant problem. To assess a sorption effect in the field, two of the piezometers were fitted with a teflon sampling tube adjacent to one of the polyethylene tubes so that duplicate samples could be obtained from the same point.

The piezometers were constructed with either 7 or 23 sampling points. The points were spaced at 20 cm intervals from 0.5 m below the top of the centre stalk to either 1.7 m or 4.8 m. The centre-stalk of the 7 point piezometer served as a shallow water table piezometer which could be used to monitor changes in the water table during injection. The 23 point piezometers were not fitted with an additional shallow water table piezometer.

The injection well was constructed with 31 mm (2 in) O.D. PVC pipe fitted with a threaded No. 10 slot commercial well screen (Timco). Threaded PVC caps were fitted to the top and bottom of the well, and provisions were made in the top cap to insert 4.4 mm (1/4 in) O.D. teflon tubing into the well for injection.

The injection well and piezometers were installed in the field during July, 1984, at locations shown in figure 3.2. The piezometers were labelled as the B series from B1 through B17 to distinguish them from the existing grid network. A schematic of the final installations, showing the shallow and deep piezometers and the injection well, is shown in figure 3.3. All installations

were carried out by jetting using a Cobra drill and native groundwater. Steel casing was first jetted to the desired depth, and the piezometer or well was then placed inside the casing. The casing was then removed to allow sand to collapse around the sampling ports or well screen.

Undisturbed cores were retrieved using the Cobra drill and 31 mm (2 in) diameter aluminum tubing during the installation of piezometers B4, B13, B14, and the injection well. The core lengths and locations are indicated in Table 3.1 below.

Table 3.1: Core Lengths and Locations from the Borden Site

<u>Core no.</u>	<u>Location</u>	<u>Length (m)</u>
1	injection well	2.9
2	B13	5.2
3	B14	1.5
4	B 4	1.5
5	1.2 m W of injection well	1.5

The cores were obtained for laboratory use to assess sorptive and hydrogeologic properties of the sand, and for biodegradation studies.

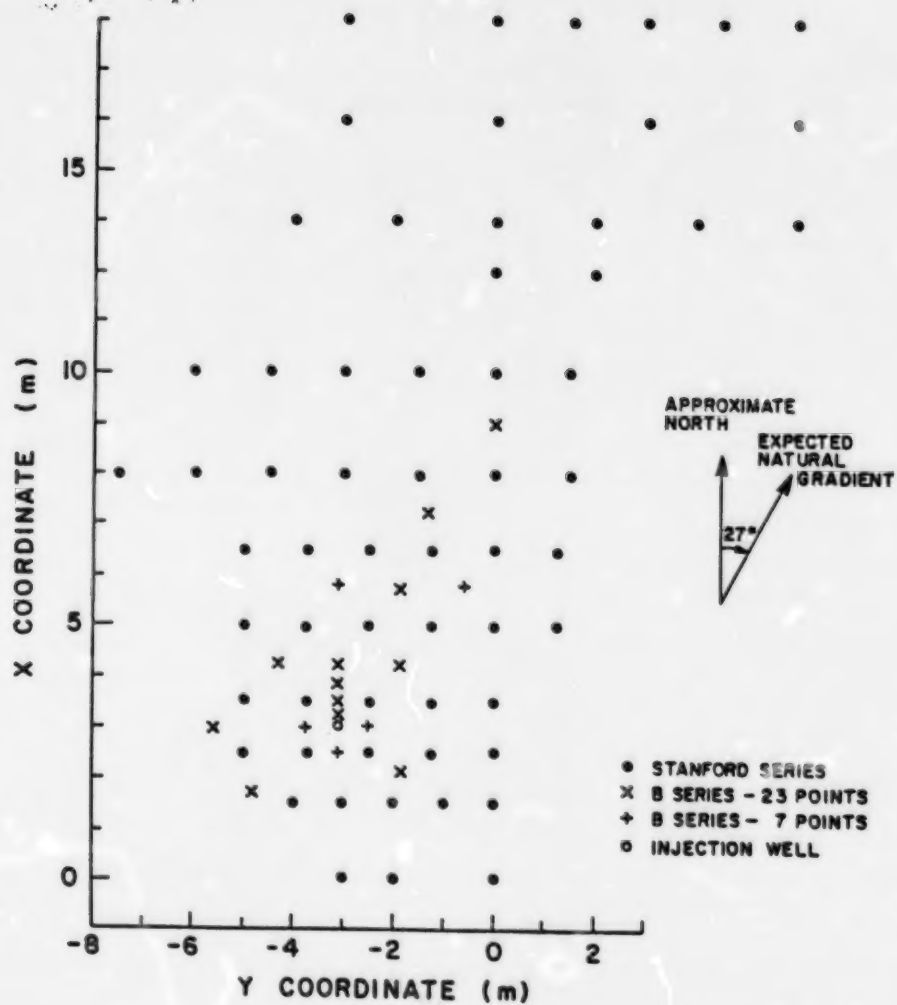


Figure 3.2: Locations of multilevel piezometers. Shown is a portion of the Stanford multilevel network, and B series multilevels and the injection well installed for the present study.

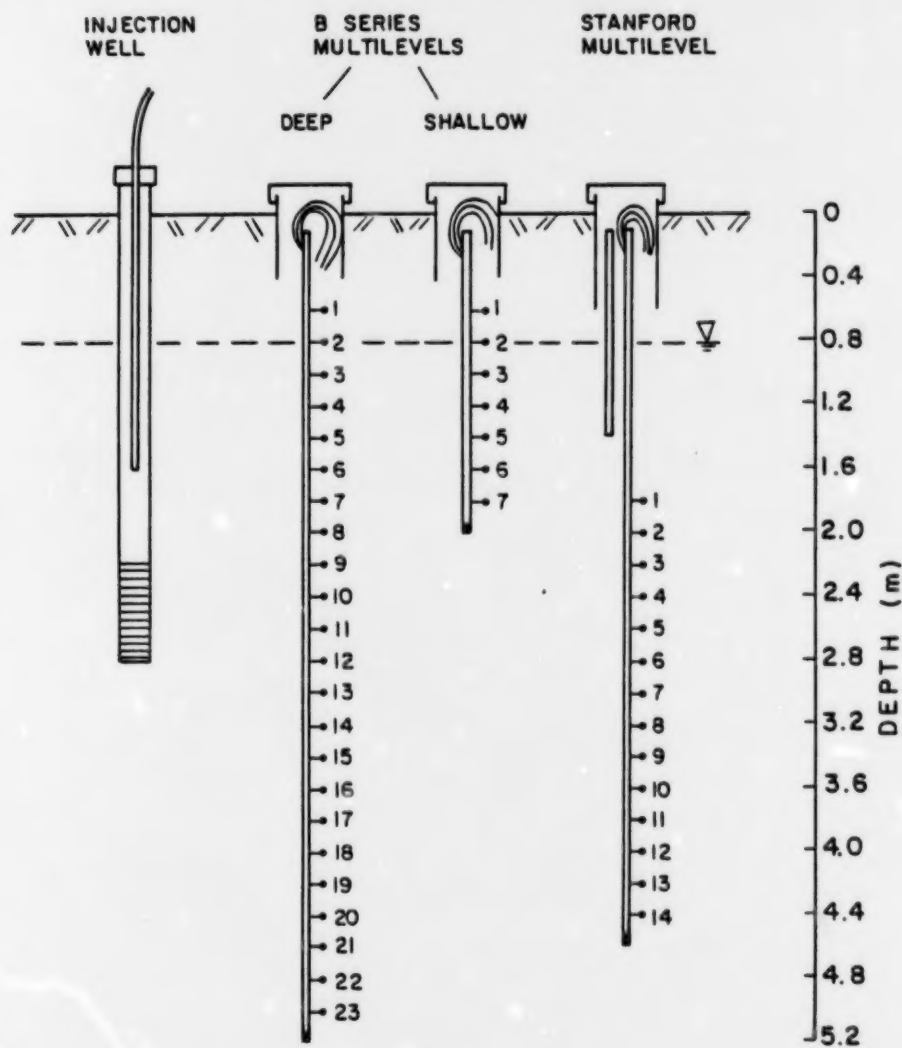


Figure 3.3: Injection well and piezometer installations.

3.6 Injection Composition

The chemical constituents of choice for the injection experiment were benzene, toluene, p-xylene, m-xylene, and o-xylene. These compounds are all single aromatic hydrocarbons which are relatively soluble in water, and are common constituents of refined petroleum products such as gasoline. Among other hydrocarbons they are relatively mobile in groundwater. However, with the exception of m and p-xylene, their individual mobilities are significantly different from one another when observed in laboratory column experiments.

All of these hydrocarbons have been shown by others to degrade biologically in the presence of water and oxygen (Hopper, 1978; Gibson, 1976). However, the relative rates of biodegradation are not well understood, especially in groundwater environments. All of the three xylene isomers were included in the injection experiment to detect differences, if any, in the biodegradation rates of very similar compounds. O-xylene, in particular, was of interest because it has been shown to degrade in the presence of other carbon substrates, but cannot be degraded as a sole carbon source (Jamison, 1976). Any decrease in the total mass of a constituent would infer that biodegradation or irreversible sorption had occurred. Biodegradation can be distinguished from sorption by confirming the presence of biodegradation products. Many products have been identified during BTX biodegradation in laboratory studies (Abbott and Gledhill, 1971).

It was desired to produce a groundwater plume with hydrocarbon concentrations which met the following constraints:

- * each constituent should be easily detected in the laboratory over a concentration range of approximately three orders of magnitude
- * the concentrations should reflect a range which might be encountered in a realistic setting
- * they should be easily produced using a feasible injection system
- * they should be low enough to avoid toxic effects on subsoil microorganisms (less than 10 mg/L total BTX was desired)
- * they should be high enough to produce noticeable effects of mass losses produced by biodegradation, should biodegradation occur

It was also decided to add chloride as a conservative non-reactive tracer to permit comparisons of the behaviour of the hydrocarbons with the natural flow regime.

In light of these constraints it was concluded that the compounds should be injected into the ground to produce a plume with concentrations in the order of 3 mg/L benzene, 2 mg/L toluene, 1 mg/L of each xylene, and 1000 mg/L chloride. These concentrations are well below the individual and grouped solubility limits for the compounds, and laboratory tests had indicated that these concentrations could easily be achieved by mixing with water within one to two hours. However, because the hydrocarbons are relatively volatile and exhibit sorptive properties, it was known that the final concentrations would depend upon an appropriate injection system design.

3.7 Injection System

The injection system was designed to meet the following criteria:

- * deliver 2000 L of water to the injection well at 1.5 L/min
- * capable of mixing the chemical constituents on site
- * produce a final BTX concentration of about 3:2:1:1:1 by weight
- * minimize volatilization and sorption losses prior to injection
- * ability to control flow rates and meter the flow
- * ability to sample water immediately before the injection well

The final design shown schematically in figure 3.4, used a 2000 L capacity flexible PVC bag as a water reservoir. The bag was shown to have a high sorptive capacity with respect to BTX, and thus the hydrocarbons could not be mixed directly in the bag prior to injection. Instead, a mixing system was designed using two 200 L tanks lined with collapsible polyethylene bags. The BTX and chloride could be added to the tanks and mixed, and then sealed to inhibit volatilization. This spike solution could then be metered into a glass flask where it would be mixed with reservoir water, and metered through a teflon and glass flowmeter to the injection well.

The spike solution required BTX and chloride concentrations approximately 10 times greater than the final desired concentration. Laboratory tests indicated that these concentrations could be achieved in approximately 1 1/2 hours, although some loss of BTX would occur. It was found that injecting approximately 30 mL of a 1:1:1:1:1 by weight solution of BTX into 120 L of water, followed by mixing, produced a spike solution with a BTX weight ratio of about 3:2:1:1:1, as was desired.

The entire injection system was tested in the laboratory to establish optimum flow rates and ensure that the final desired concentration would be achieved. It was assumed and observed that gradual mass losses would occur during the mixing and flow through the system. However, these losses which amounted to an approximate 25% reduction in concentration over 24 hours were not considered critical to the injection's success because the concentrations entering the injection well could be easily and frequently sampled through time. Thus the total mass of each constituent entering the well would be known.

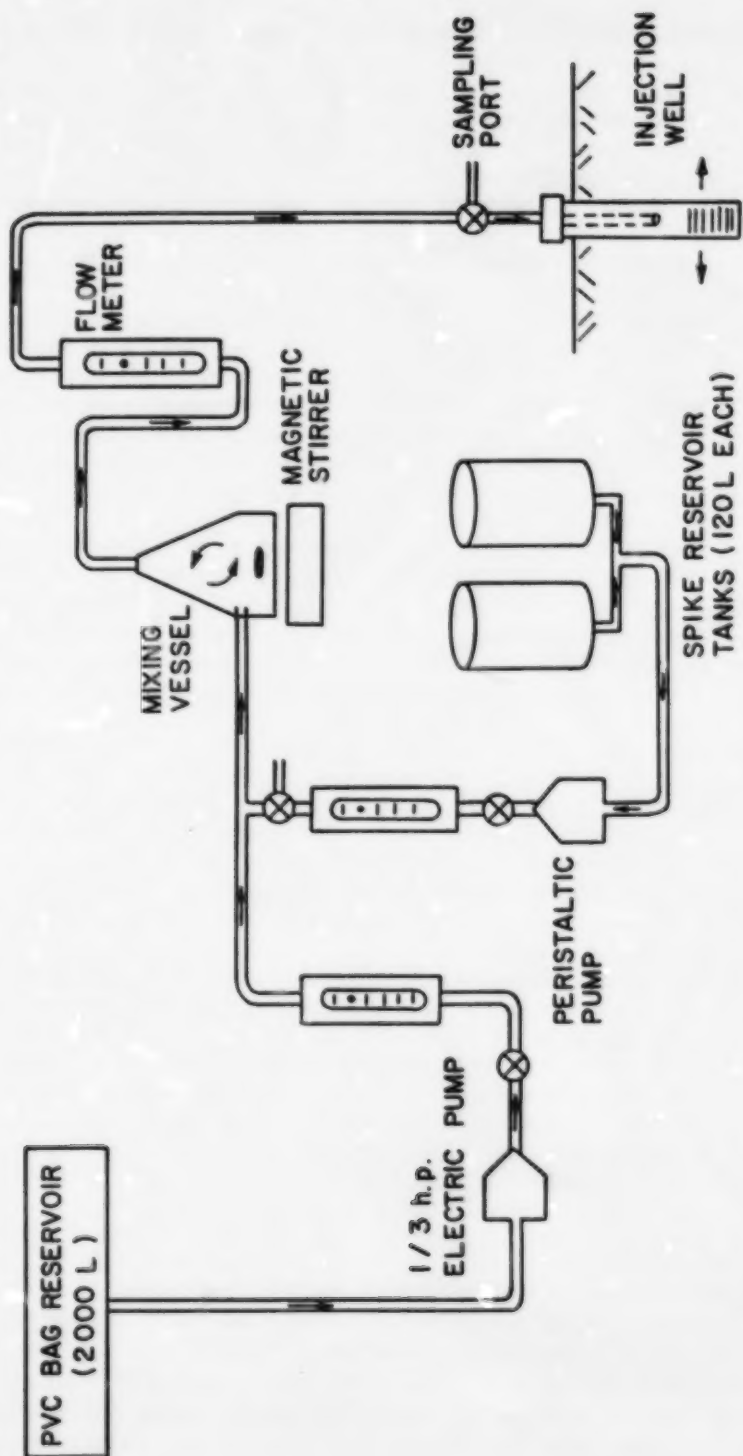


Figure 3.4: Schematic of the BTX injection system.

3.8 The Field Injection

The injection system, chemicals, and sampling equipment were transported to the Borden site on August 8, 1984. Water for the 2000 L reservoir was obtained by pumping from a well located approximately 100 m from the injection well. The system was assembled and a trial injection without chemical additions was performed for 1 hour. This was done to adjust the flowmeters and ensure the system was operating properly. Water levels were monitored during the injection, and the water table appeared to reach equilibrium quickly.

The following day the spike tanks were each filled with 120 L of reservoir water. A total of 1.861 kg of sodium chloride was added to each tank and mixed for approximately 15 minutes using an impeller and shaft mounted to a small electric motor. A syringe and teflon tube were then used to inject 27.6 mL of a 1:1:1:1 by weight BTX solution into each tank while mixing. Mixing continued for 1 1/2 hours. Each polyethylene bag was then sealed. The injection commenced at 1:08 p.m. on August 9 and continued for 21 hours til 10:08 a.m. the following day. The injection flow rate was maintained at 1.43 L/min. A total of 1800 L was injected.

Throughout the injection samples were retrieved in sealed hypovials every 15 minutes from the injection well, hourly from the spike tanks, and every half hour from piezometers B6 and B7. In addition, periodic measurements of dissolved oxygen and temperature were made of the injection water, and water level measurements were made in the injection well and several nearby water table piezometers. A summary of pertinent results from the injection is presented in Tables 3.2 and 3.3.

Table 3.2: Preliminary Injection Data

Injection Flow Rate	1.43 L/min
Total Volume Injected	1.8 m ³ = 1800 L
Duration of Injection	21 hours
Average Dissolved Oxygen	
Concentration of Injection	
Water	1.36 mg/L
Average Temperature of	
Injection Water	23.7°C

Of concern during the injection was that the water level within the injection well continually rose, and approached the top of the well casing. Water levels in nearby piezometers did not indicate significant mounding within the

Table 3.3: Preliminary Calculations of Mass of Chemicals Injected

<u>Chemical</u>	<u>Calculated Mass</u>	<u>Average Injection Concentration</u>
Benzene	4.25 g	2357 µg/L
Toluene	3.16 g	1750 µg/L
P-xylene	1.94 g	1075 µg/L
M-xylene	1.96 g	1087 µg/L
O-xylene	2.31 g	1282 µg/L**
Chloride	2.30 Kg as Cl ⁻	1280 mg/L

* actual benzene values may be slightly lower than reported due to sample contamination by hypovial septa. See section 3.10 of text.

** the chloride concentration was back-calculated from the known mass of chloride injected. The mass injected is the sum of the mass added to the injection water (3.722 kg as NaCl) and the mass in the injection water prior to chemical additions (25 mg/L).

aquifer. It was hypothesized that clogging at the well screen had occurred, possibly due to the precipitation of iron oxyhydroxides from the reservoir water. This effect did not appear to affect the concentrations or distribution of chemicals within the groundwater plume.

3.9 Sampling Procedures

Sampling for dissolved volatile organics from piezometers requires a system which minimizes the contact time of the sample with air, and minimizes the sorption of the organics onto sampling apparatus. If the samples cannot be analyzed immediately, they must be retrieved in clean non-sorbing sample vials which can be sealed with no air inclusions. Fortunately, procedures and apparatus developed for the Stanford-University of Waterloo injection experiment proved satisfactory for the present study.

The multilevel piezometers are easily sampled using a manifold system which allows the simultaneous collection of groundwater from up to 14 sampling points. The tubes from a multilevel are connected to the manifold, and a peristaltic pump is used to create a common vacuum. Water is consequently withdrawn from each tube into separate 15 mL glass hypovials. The hypovials are flushed with approximately 50 mL of sample water to remove standing water from the piezometer tubes and to ensure that the final sample has not contacted air. The sample vials are left brimming full with water. They can be quickly sealed with teflon lined septa and aluminum caps, leaving no air trapped within the sample.

The manifold also allows the collection of two sample vials from one of the multilevel tubes. The feature provides 'duplicate' samples for an assessment of laboratory and field quality control. The samples are not true duplicates, however, because the two vials are filled one after the other from the tube, rather than from a split common sample.

Previous studies by Stanford and the University of Waterloo had shown that the procedures provide representative samples of volatile organics from the multilevel piezometers (Mackay et al., 1983a). The volume of water removed from the soil at each sampling point is not sufficient to cause short-circuiting between points, and sorption is reduced to a minimum.

In using the manifold at a multilevel, a set of samples was first retrieved for chloride determinations. These were collected in hypovials and then transferred to plastic bottles. The multilevel was then resampled to obtain hypovial samples for BTX. The BTX samples each received 0.1 mL of 10% sodium azide as a preservative prior to sealing. All samples were labelled and recorded on site, and stored in a cooler with ice packs until arrival at the laboratory in Waterloo. A typical multilevel was sampled within approximately one half hour. By using two manifolds the entire plume could be sampled by three to four persons within two days. These sampling sessions provided data for 'snapshots' of the plume, so that the progress of the plume could be assessed at discreet intervals over the course of several months.

The need to add azide as a preservative was not established until after the first snapshot sampling session in August. Tests conducted at that time had shown that rapid losses of BTX could occur within a few days storage at 4°C due to biodegradation. Sodium azide inhibited the native groundwater microbial activity. Because azide was added to all samples following the initial August snapshot, those analytical results are likely to be more precise and accurate than the August data. An assessment of laboratory standards and field replicate samples is being conducted to establish precision and accuracy.

Chloride results for the August data are also likely to be less accurate than later data. This is because separate chloride samples were not collected until the second snapshot in September. Initially, chloride determinations were made on the same water samples collected for BTX analyses. This procedure proved unsatisfactory, however, due to chemical interferences during analysis which affected results.

Dissolved oxygen measurements were taken from selected multilevel piezometers following each snapshot sampling session. The measurements were taken from alternate tubes of each chosen multilevel to provide a vertical cross section of dissolved oxygen concentrations along the length of the BTX and chloride plumes. The Winkler method was employed using syringe techniques. It was preferred over other methods because it has a relatively high accuracy at low dissolved oxygen concentrations. The entire procedure was performed in the field, and the measurements for the cross section could usually be completed within one and one-half days.

In addition to the snapshot sampling program, selected points at two or more multilevels were sampled at weekly or twice weekly intervals for BTX and chloride determinations. This was done to establish breakthrough data for the plumes as they migrated. The resulting breakthrough curves could then be used to assess sorption and retardation of the compounds in the subsoil.

3.10 Laboratory Procedures

The need to analyze a large number of samples within one to two weeks necessitated the development of rapid and efficient laboratory procedures. The procedure of choice for the measurement of BTX concentrations was a solvent extraction step followed by analysis using gas chromatography. Similar procedures had been used in the Stanford-University of Waterloo study to determine concentrations of halogenated organics in hypovial samples (Mackay et al., 1983a) and by Glaze et al. (1983) to determine benzene among other organic concentrations in water.

The solvent extraction method is a sample preparation step which effectively concentrates dissolved organic compounds in a measured amount of organic solvent. In the present study, the extraction was performed using syringe techniques within the sample hypovial to minimize losses. In the early part of the study, pentane was used as the organic solvent, and a small amount of either sodium sulphate or sodium thiosulphate was added as a 'salting out' agent to enhance the extraction process. The procedure was modified after analysis of the August samples. to improve accuracy. Hexane was used instead of pentane, and the 'salting out' agent was omitted. A detailed description of the latter method used in conjunction with gas chromatography is presented in Appendix D.

The solvent extraction and gas chromatography were performed at the University of Waterloo. Two Hewlett-Packard gas chromatographs (5840A, 5790) equipped with electronic integrators were used simultaneously to run samples. As a quality control measure, standards of BTX compounds were prepared and extracted in hypovials and run every tenth sample. Sample concentrations were output from the integrators, reviewed for errors, and then placed on data sheets for later entry into the computer. For all samples collected in August, a problem was encountered in resolving benzene peaks due to contamination from the hypovial septa. The septa contained compounds, which, when punctured, dissolved into the solvent and produced substantial interfering peaks on the gas chromatograph. This tended to cause higher than actual values for benzene concentrations for the injection and August snapshot data. By reducing the run time to 5 minutes, using the hexane extraction procedure, and boiling and baking the septa prior to use, the contamination problem was solved and accuracy improved.

Chloride samples were analyzed using an automated wet chemical procedure (Technicon Industrial Method No. 99-70 W/B) on a Technicon Autoanalyzer II. The procedure involves the release of thiocyanate ions into solution in proportion to the sample chloride concentration. In the presence of ferric ions, a highly coloured ferric thiocyanate forms which can be quantified using spectrophotometry. The system requires approximately 1 mL of sample per analysis, and can process up to 60 samples per hour.

3.11 Data Analysis and Preliminary Results

Since the injection, five snapshot sampling sessions have been completed, and over 3200 samples have been analyzed for BTX and chloride. The snapshot dates and respective days after injection are presented in Table 3.4. Preliminary results indicate that the slug has travelled in the down-gradient direction, and that a distinct fingering of the slug has occurred along horizontal layers of the aquifer material. Hydraulic conductivity determinations are currently being performed on core samples from the site to assess the relationship between the observed fingering pattern and the vertical conductivity contrasts.

Table 3.4: Snapshot Sampling Information

Snapshot No.	Sampling Date (1984)	Days After Injection	No. BTX Samples Collected
1	13 August	3	440
2	5, 6 September*	26	593
3	2, 3 October	53	701
4	30 October -1 November	81	775
5	26, 27 November	108	771

* A separate chloride 'snapshot' was obtained on 11, 12 September.

All snapshot data have been entered into the IBM 370 computer at the University of Waterloo in a form amenable to analysis using Fortran and Watfiv computing languages. At present, the analysis has concentrated on assessing the horizontal aspect of the slug to define the position, relative retardation, and masses of the chemical constituents.

In the horizontal analysis each set of snapshot data is first reduced using trapezoidal quadrature to derive average chemical concentrations at each multilevel piezometer. The quadrature is an integration procedure wherein the calculated concentration at each multilevel represents the mass sum of the vertical concentration profile. The average concentrations and respective X-Y co-ordinates are then input into the SURFACE II computing routine to derive two-dimensional plots of the plumes for each chemical constituent.

SURFACE II is a computer package which interpolates the initial data to a regular grid prior to plotting. The grid can be stored and used in other routines to calculate moment estimates of total mass, centre of mass, and dispersion.

Horizontal plots of the vertically averaged data for the third snapshot October 2 and 3, 53 days after injection, are presented in figures 3.5 through 3.10. The plots were produced by SURFACE II using a relatively dense grid spacing of 0.3 m. Plots of other snapshot data remain to be constructed, and will be discussed in a future report.

Comparison of the October plots illustrate the effects of retardation and fingering, and provide qualitative evidence that losses of mass have occurred for some of the constituents. Chloride, which acts as a non-reactive tracer, has travelled the furthest of the constituents, whereas all of the BTX have been significantly retarded. Benzene appears to be retarded the least, followed by toluene and the xylenes. Fingering of the slug is especially evident in the benzene plot, which shows a frontal lobe adjoining the bulk of the benzene plume. A comparison of the m and p xylene plots (figures 3.8 and 3.9) suggests that a substantial loss of mass of m-xylene has occurred. Both m and p xylene were initially injected at almost identical concentrations, yet after 53 days the mass of m-xylene is substantially less than that of p-xylene.

The 1984 field snapshot sampling program and laboratory analyses have been completed. The slug has continued its migration down-gradient and is presently in a poorly monitored area where the grid spacing of multilevel piezometers is only 3 m. No further snapshot sampling is planned for the winter months. However, several piezometer points are still being monitored at weekly intervals, weather permitting, in attempts to establish breakthrough curves for the constituents.

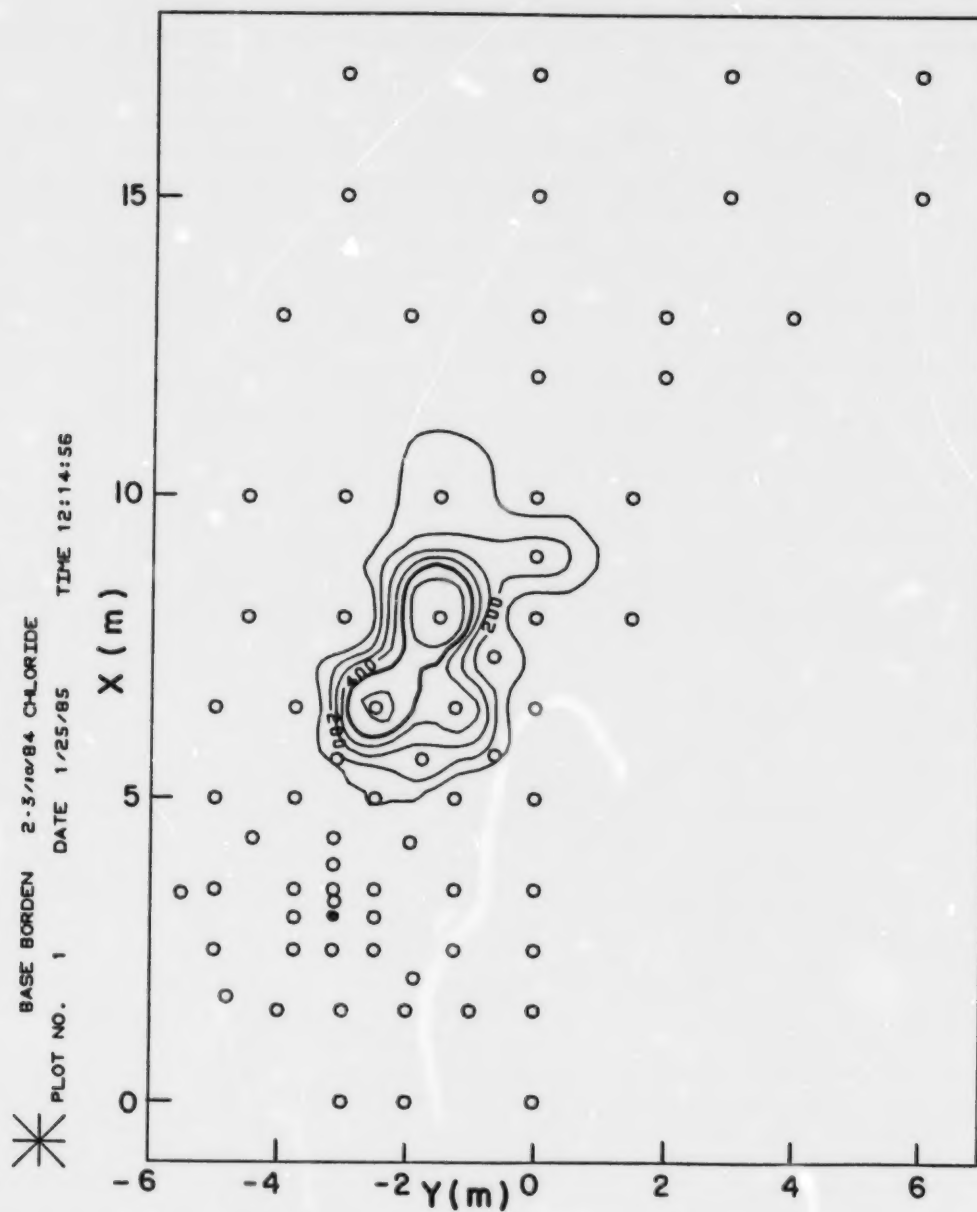


Figure 3.5: Chloride contour plan 53 days after injection.

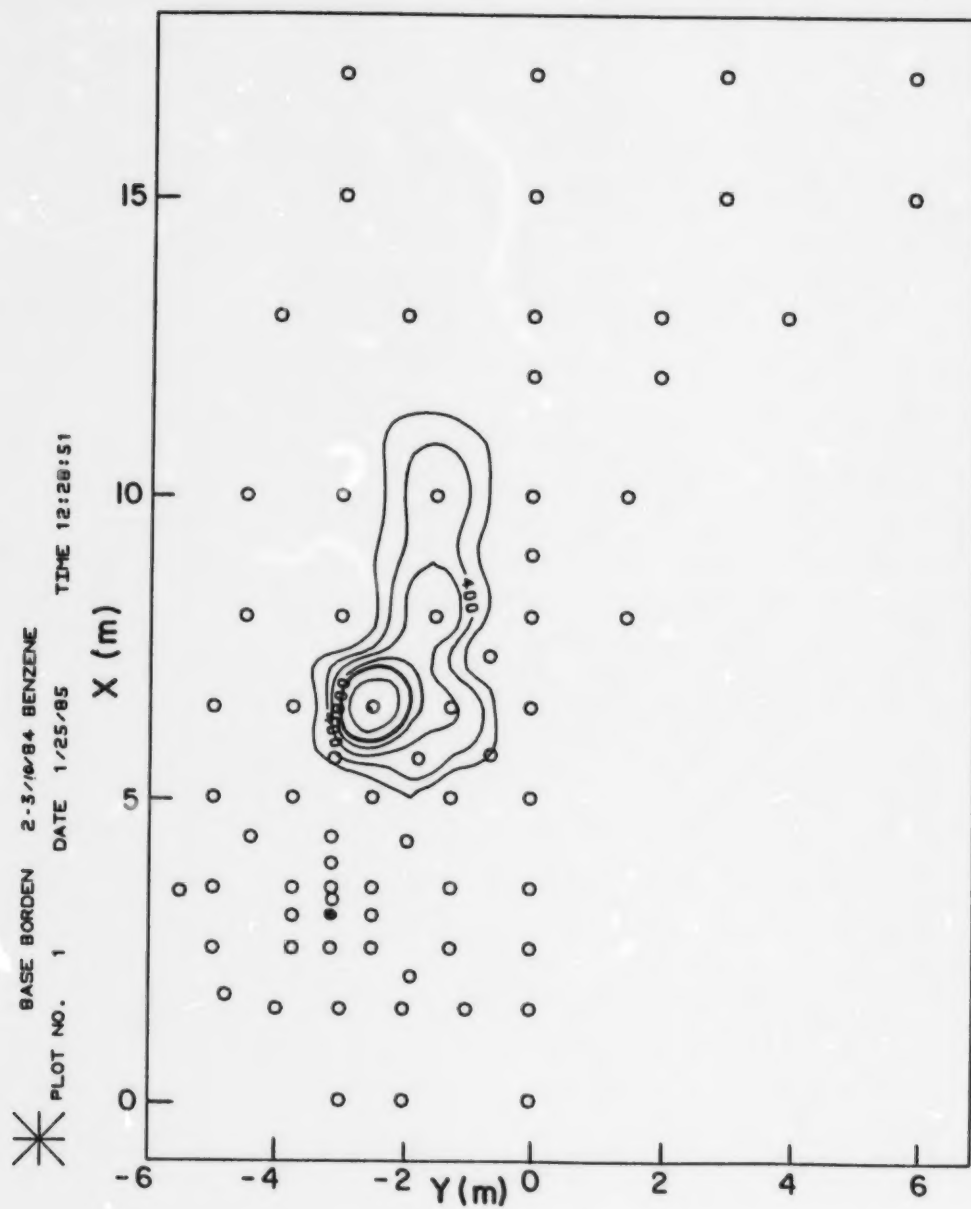


Figure 3.6: Benzene contour plan 53 days after injection.

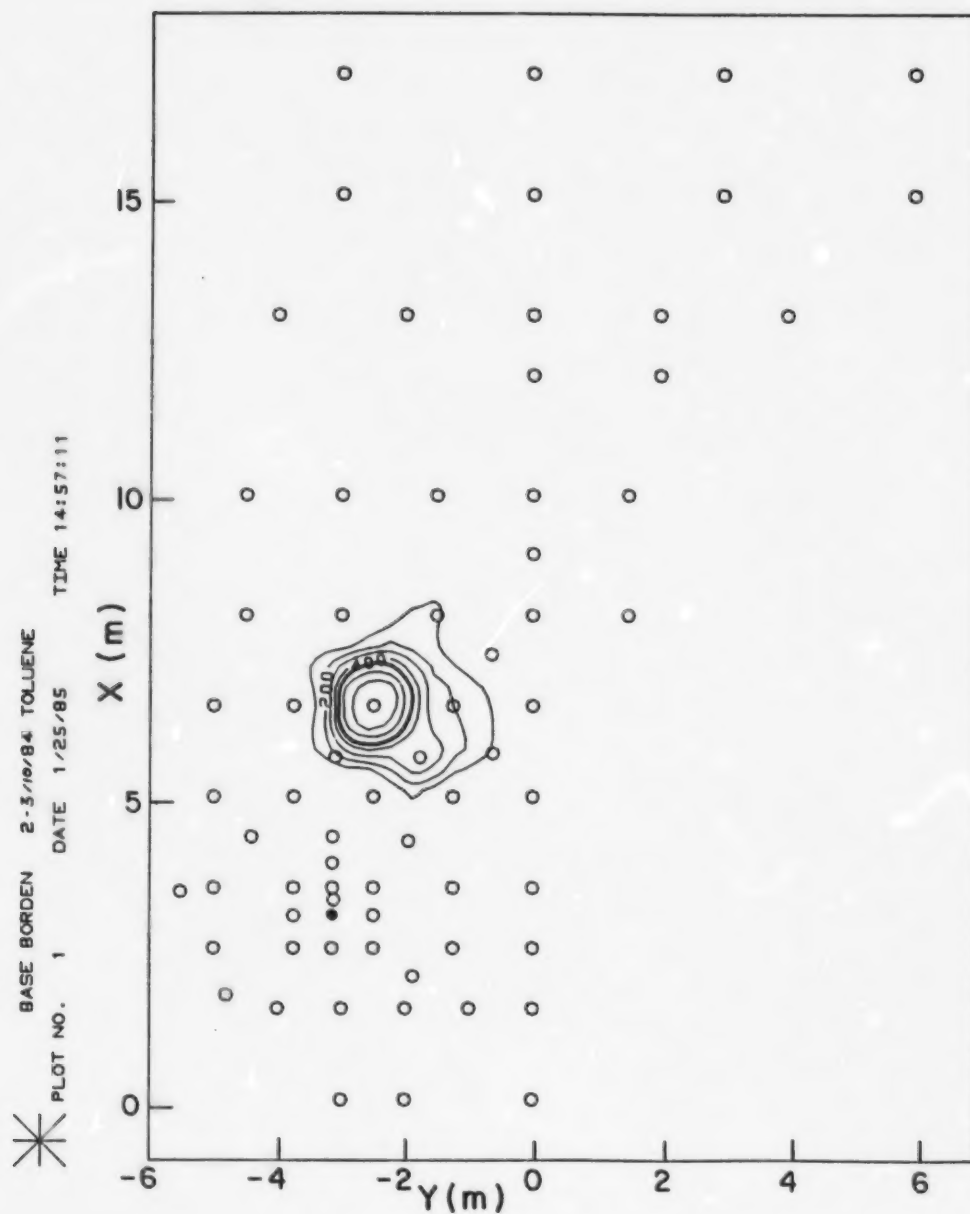


Figure 3.7: Toluene contour plan 53 days after injection.

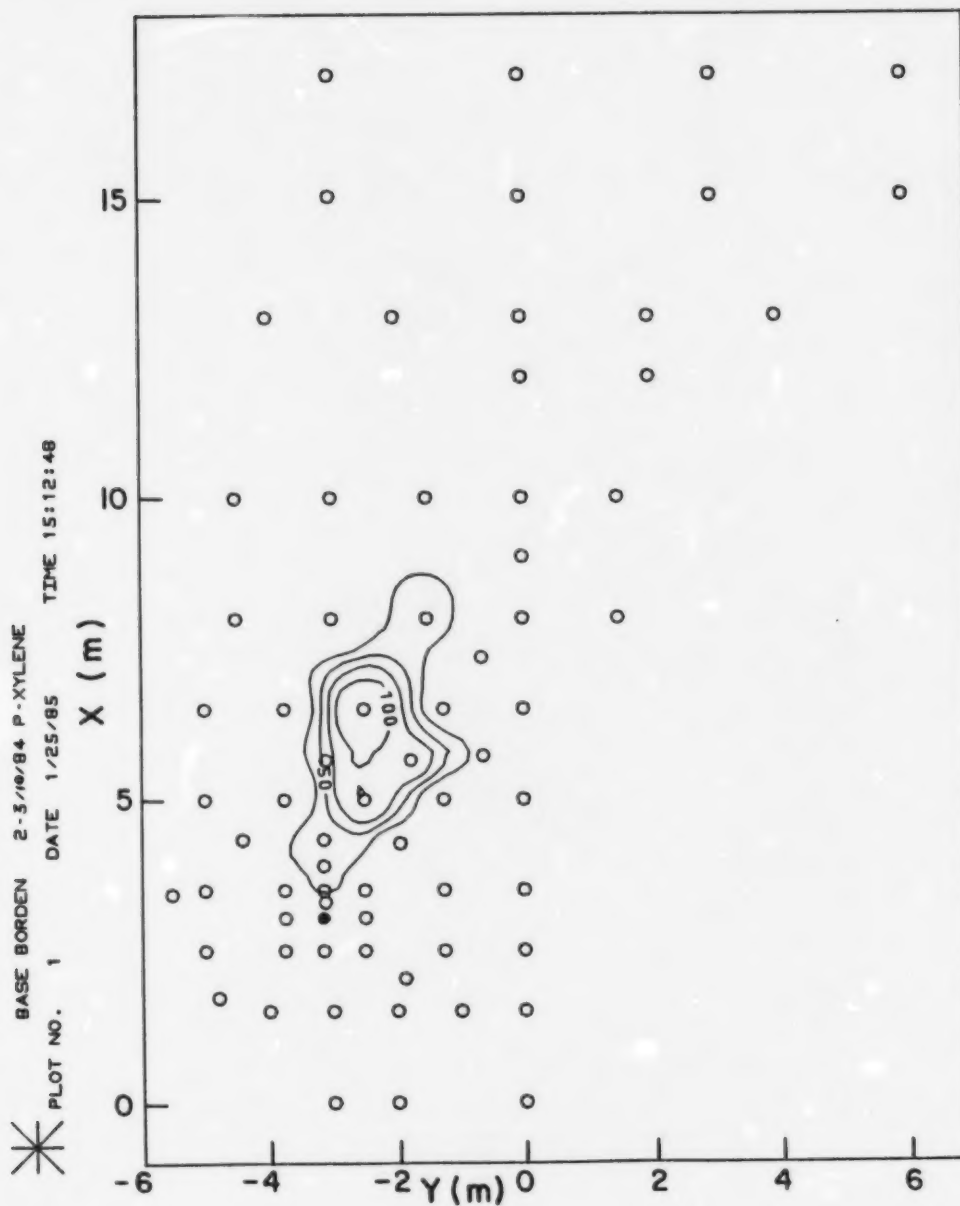


Figure 3.8: P-xylene contour plan 53 days after injection.

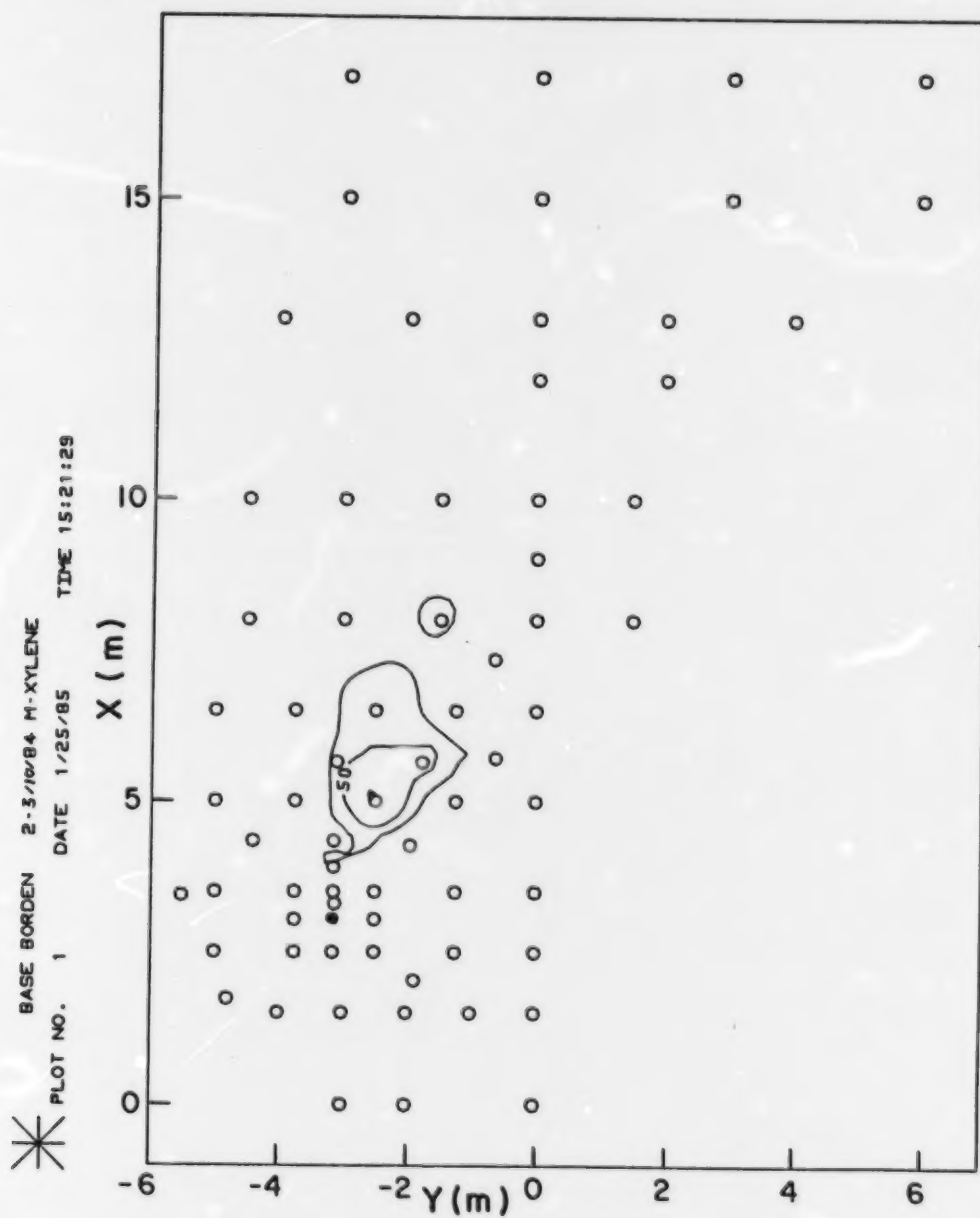


Figure 3.9: M-xylene contour plan 53 days after injection.

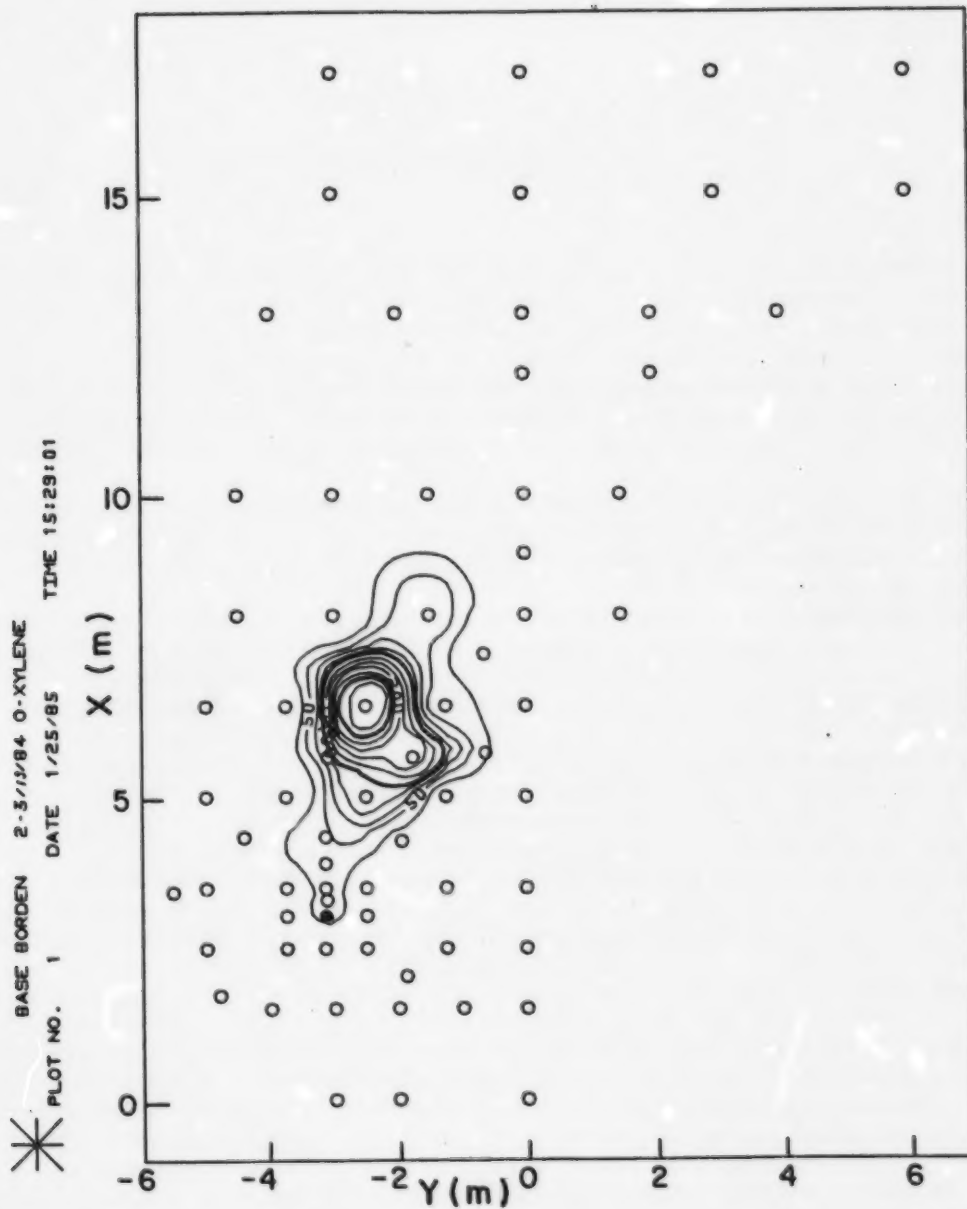


Figure 3.10: O-xylene contour plan 53 days after injection.

BIODEGRADATION STUDIES

In Phase I, the goal was to test, in the laboratory, the biodegradability of BTX under conditions approximating those at the Borden site. The results of the field test could then be used to assess the efficacy of predictions based on simple laboratory tests. It was necessary, however, to develop a novel analytical technique for BTX which caused a minimum disturbance to experimental systems. This analytical development necessitated the postponement of the biodegradation studies to Phase II.

This technique involves establishing numerous sealed hypovials containing aquifer material with its microbial population and synthetic groundwater spiked with trace organics. The vials are then incubated at 10°C, a typical groundwater temperature at the field site. Some vials are sterilized as controls, so that the affects of biodegradation can be isolated from other processes. Small groundwater samples (100 ul) are to be periodically removed through a special seal (mini-inert valve) so that only a minimum headspace is created. These samples are then analyzed by high performance liquid chromatography (HPLC) to monitor, over time, both the disappearance of BTX and phenol and the appearance of other organic products. When other products are found, they will be characterized by GC and GC/MS methods.

The newly-established HPLC procedure involves adding 1 ul of an interval standard solution to the 100 ul sample in a mini reactivial. A 20 ul aliquot is injected onto a Supelco LC-18, 3 um by 15 cm HPLC column with elution by an isocratic gradient of 80% acetonitrile - 20% water. BTX are chromatographed within 5 minutes with a detection limit of about 0.1 ppm using an ultraviolet detector set at 210 nm.

This technique is best-suited for examining the processes of biodegradation with initial BTX levels of tens of ppm. The 100-fold differences between initial starting concentration of BTX and the detection limit allows the determination of biodegradation rates. As such it complements the GC procedure established for assessing lower levels of BTX. It is currently being applied to the biodegradation studies as part of Phase II of this research project.

PHASE-II PROJECTS

5.1 Introduction

Objectives for Phase II are to provide:

1. An evaluation of the migration of BTX through an actual shallow sand aquifer including an assessment of contaminant attenuation by natural biodegradation and sorptive retardation processes.
2. An evaluation of various methods for estimating biodegradation rates and sorptive retardation in part through comparison of results from such methods with the results of the natural gradient injection experiment.
3. An evaluation of various nutrient addition methods aimed at enhancing BTX biodegradation in situ in shallow sand aquifers.

The most significant results expected at the end of Phase II include:

1. An evaluation of the migration of BTX through an actual shallow sand aquifer including an assessment of contaminant attenuation by natural biodegradation and sorptive retardation processes.
2. An evaluation of various methods for estimating biodegradation rates and sorptive retardation through comparisons of results from such methods with the results of the natural gradient injection experiment.
3. An assessment of BTX mass loss via "irreversible" sorption onto sandy aquifer materials--is it a significant attenuation mechanism?
4. A comparison of the methods of estimating sorptive retardation in sandy materials having organic carbon contents varying from 0.02 to 1%--can one method be recommended?
5. An evaluation of possible nutrient additions which would stimulate in situ microbial degradation of BTX and phenol--which method should be tested at the field site in 1986?

5.2 Evaluation of Methods for Measuring Retardation

The activities proposed in this section are based on the results obtained during the initial year of the study, and more specifically, are designed to address the particular difficulties and uncertainties outlined in the October 1984 progress report. The work will serve three general objectives:

1. to obtain an improved understanding of the geochemical factors affecting the transport of BTX in hydrogeologic regimes.
2. to obtain an expanded data base that would allow for a more reliable extrapolation of the results to geological materials covering a range in physical and chemical properties.
3. to arrive at a more substantial basis for identifying the limitations and advantages of the various test procedures, and ultimately arriving at recommended procedures for a variety of hydrogeologic regimes.

5.3 Natural-Gradient Field Test

The injection of BTX-contaminated groundwater at the Borden site was successfully completed in August 1984 and the migration of these components is being monitored through April 1985. This experiment provides a field evaluation/verification of the dispersion predictions, the sorption determinations and the extent of natural biodegradation in this shallow sand aquifer. Monitoring of the contaminant plume will continue in the spring of 1985 and the contaminant concentrations will be mathematically modelled to assess the extent and predictability of advection dispersion, sorption and transformation processes influencing BTX migration. Dispersion information from other projects ongoing at the same site will be combined with data for the conservative tracer (Cl^-) included in the BTX injection. Laboratory sorption and biodegradation data will also be incorporated to assess their applications to field situations. Models will be based on the estimated statistical moments of contaminant distributions as well as on their 2 dimensional distribution. At the end of phase 2, the field experiment will provide a preliminary evaluation of the ability of laboratory and literature data to describe the migration and attenuation of BTX in a shallow sand aquifer.

Over 20,000 solute concentration data will be obtained from the field experiment. A major task in phase 2 is to manipulate this data to obtain an accurate, 3-dimensional picture of the evolution of solute concentrations over time and to compare these with the model-generated distributions based on literature, lab, and field estimates of dispersion, sorption and biodegradation rates. The data management system and calculation procedures have been established in phase 1, but most of the plume mapping and interpretation will occur in phase 2.

5.4 Biodegradation and Remediation Using Enhanced Biodegradation

In phase 1, the natural microbial population at the tracer test site will be described and high performance liquid chromatograph analytical techniques required for phase 2 studies will have been established.

In 1985, the microbial population in aquifer core material, through which the BTX plume has migrated, will be again assessed. The ability of bacteria to degrade BTX, both aerobically and anaerobically, will be compared to that of the "pre-plume" aquifer core population. This will establish the degree of microbial adaption to BTX degradation that has occurred. If adaption is demonstrated, then biodegradation rates, normally assumed constant in predictions, should be variable and dependent upon the degree of adaption. In that case, attenuation of early-arrival contaminants may be minimized while purification of residuals may be more rapid than predicted.

The processes and rates of biodegradation at the field site will be evaluated during phase 2 through laboratory batch tests using methods described in the phase 1 proposal. The validity of such laboratory estimates of biodegradation will be tested against the BTX concentration changes (mass decrease) found in the tracer test.

The "balanced nutrient" addition method for in situ aquifer remediation will be evaluated in flask experiments in the laboratory, as described in the phase 1 proposal. Degradation of phenol as well as BTX will be assessed. The most successful addition method will then be applied at the tracer injection site to remediate a BTX plus phenol plume that will be injected in the spring of 1986. It may be possible, in phase 3, to evaluate other remedial methods (peroxide or O_2 addition, for example) at the field site as well.

5.4.1

Proposed Activities

1. Many of the difficulties associated with the interpretation of the results obtained in the first year of the study can be attributed to the low retardation of BTX in Borden sand. In particular, with the retardation approaching 1.0 (unretarded) all methods gave similar values and thus no basis for assessing the relative accuracy of the methods. In addition, the low retardation values contributed to the difficulty encountered in obtaining reproducible batch results, and an inability to evaluate possible kinetic effects from the results of the column procedures. Having conducted the tests on only one material provided little basis for extrapolation of the results or for the selection of the most appropriate correlation equation.

As a major activity of the second year, retardation coefficients will be determined in additional aquifer materials. The methods used will include the correlation equations, batch isotherm procedures, and some laboratory columns. The major criterion used in selecting the additional materials (sites) will be the organic carbon content of the geologic material. Two sites will be selected that have organic carbon contents

ranging between that of the Borden aquifer (about 0.02%) and about 1.0% (dry weight basis). At the present time we have access to numerous sandy aquifer materials in southern Ontario, and though site selection may be time consuming, we anticipate that the required materials will be available.

The experimental procedures will be virtually identical to those used in the initial year of the study.

2. Experiments will be conducted to identify the cause of the apparent loss of mass observed in the results of the initial column experiments. Initially, tests of the experimental apparatus and procedures will be conducted. Should these prove not to be the cause, further testing of the geological materials will be required. In particular, specific tests for evidence of "irreversible" uptake will be undertaken. These tests could involve the sectioning and analysis of the column materials following the passage of a tracer slug.

The implications of irreversible uptake are important in that it would suggest that the mobility of BTX in aquifer materials is not as great as the preliminary results at Borden suggest, and further, that a simple retardation factor is not an adequate parameter for evaluating mobility. Though a preliminary examination of the loss of mass will be undertaken in the second year of the study, detailed studies would be designed on the basis of the preliminary results and would be undertaken during the third year.

GLOSSARY OF CONTAMINANT HYDROGEOLOGY TERMS

Advection. The process by which compounds are transported in groundwater by the bulk motion of the flowing groundwater.

Chemical Precipitation. The process whereby dissolved compounds or elements combine to form a solid phase, thus removing mass from solution.

Chemical Transformation. The process in which compounds, especially contaminants, are chemically changed by non-biological processes, such as hydrolysis, oxidation, and reduction.

Conservative Solute. A dissolved compound which does not undergo retardation processes and so moves at the same velocity as the groundwater. Chloride ion is a common example. Also termed non-reactive solute.

Dispersion. The process by which dissolved compounds (solutes) spread out from the path that they would be expected to follow according to advection. Also called hydrodynamic dispersion.

Dissolution. The process whereby solid phases dissolve, adding compounds or elements to solution.

Microbial Transformation. Also termed biochemical degradation and biodegradation. The process in which compounds, especially contaminants, are chemically changed where the process is carried out by micro-organisms.

Octanol-water partition coefficient. K_{ow} An experimental value which expresses the amount of a compound that occurs in an octanol phase relative to the amount that occurs in an aqueous (water) phase when the compound is allowed to partition itself between these coexisting phases.

Retardation. The process by which dissolved compounds travel less quickly than does the bulk groundwater. Retardation results from processes such as sorption, chemical precipitation and biodegradation.

Solute. An element or compound that is dissolved in a solvent such as groundwater.

Sorption. The retardation process whereby some of the solute mass is held by the solid phase while the rest is held in solution. During advection, this process slows the compound causing retardation. In detail, the step where solute is transferred to the solid phase is (ad)sorption and the step where solute is transferred from the solid to solution is desorption.

REFERENCES

- Abbott, B.J. and W.E. Gledhill. The extracellular accumulation of metabolic products by hydrocarbon-degrading microorganisms. *Advances in Applied Microbiology*, 14:249-388, 1971.
- Bear, J. *Hydraulics of Groundwater*. McGraw-Hill Inc., 1972.
- Chiou, C.T., L.J. Peters and V.H. Freed. A physical concept of soil-water equilibria for nonionic organic compounds. *Science*, 206:831-832, 1979.
- Dance, J.T. and E.J. Reardon. Hydrogeologic studies of a sand aquifer at an abandoned landfill. 5. Cation migration in the dispersion test. *Journal of Hydrology*, 63:109-130, 1983.
- Dao, T.H., D.B. Marx, T.L. Lavy, and J. Dragun. Effect, and statistical evaluation of soil sterilization on aniline and diuron adsorption isotherms. *Soil Science Society of America Journal*, 46:963-969, 1982.
- Freeze, R.A. and J.A. Cherry. *Groundwater*. Prentice-Hall, Inc., 1979.
- Gibson, D.T. Initial reactions in the degradation of aromatic hydrocarbons. *Zbl. Bakt. Hyg. I. Abt. Orig. B.* Vol. 162, 157-168, 1976.
- Glaze, W.H., C.C. Lin, J.L. Burleson, J.E. Henderson, D. Mapel, R. Rawkey, D.R. Scott. Optimization of liquid-liquid extraction methods for analysis of organics in water, Project Report, Contract No.s CR-805472, CR-808562, USEPA/EMSL: Cincinnati, OH, 1983.
- Hansch, C. and A. Leo. *Substituent Constants for Correlation Analysis in Chemistry and Biology*. John Wiley & Sons, Inc., N.Y., 1979.
- Hopper, D.J. Microbial degradation of aromatic hydrocarbons, In: *Developments in Biodegradation of Hydrocarbons - 1*, R.J. Watkinson (ed.), Applied Science Publishers, London. 232 pp., 1978.
- Jamison, V.W., R.L. Raymond, and J.O. Hudson. Biodegradation of high octane gasoline. In: *Proceedings of the Third International Biodegradation Symposium*, J.M. Sharpley and A.M. Kaplan (eds.). Applied Science Publishers, London, 187-196, 1976.
- Kebe, J.O., G.T. Brookman, R.S. Atkins, and D.F. Unites. Report to the American Petroleum Institute for an evaluation of the natural fate of aqueous gasoline components and treatment alternatives. Task 1A - Literature Survey: hydrocarbon solubilities and attenuation mechanisms, 1984.

- Karickhoff, S.W. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere*, 10:833-846, 1981.
- Karickhoff, S.W., D.S. Brown, and T.A. Scott. Sorption of hydrophobic pollutants on natural sediments. *Water Research*, 13:241-248, 1979.
- Karickhoff, S.W. Organic pollutant sorption in aquatic systems. *Journal of Hydraulic Engineering*, 110(6):707-735, 1984.
- Kay, B.D. and D.E. Elrick. Adsorption and movement of lindane in soils. *Soil Science*, 104(5):314-322, 1967.
- Lapidus, L., and N.R. Amundson. Mathematics of adsorption in beds. VI. The effect of longitudinal diffusion in ion exchange and chromatographic columns. *J. Phys. Chem.*, 56:984-988, 1952.
- Lindstrom, F.T. and L. Boermsa. A theory on the mass transport of previously distributed chemicals in a water saturated sorbing porous medium. *Soil Science* 111(3):192-199.
- Mackay, D.M., J.A. Cherry, D.L. Freyburg, G.D. Hopkins, P.L. McCarty, M. Reinhard, and P.V. Roberts. Implementation of a field experiment on groundwater transport of organic solutes. Presented at the Groundwater Contamination Session of the 1983 National Conference on Environmental Engineering, ASCE, University of Colorado, Boulder, Colorado, July, 1983a.
- Mackay, D.M., D.L. Freyburg, M.N. Goltz, G.D. Hopkins, and P.V. Roberts. A field experiment on groundwater transport of halogenated organic solutes. Presented before the Division of Environmental Chemistry, American Chemical Society, Washington, D.C., Sept, 1983b.
- MacFarlane, D.S., J.A. Cherry, R.W. Gillham, and E.A. Sudicky. Migration of contaminants in groundwater at a landfill: a case study. *Journal of Hydrology*, 63: 1-29, 1983.
- Mingelgrin, U. and Z. Gerstl. Reevaluation of partitioning as a mechanism of nonionic chemicals adsorption in soils. *Journal of Environmental Quality*, 12(1):1-11, 1983.
- van Genuchten, M.Th., P.J. Wierenga and G.A. O'Connor. Mass transfer studies in sorbing porous media: III. Experimental evaluation with 2,4,5-T. *Soil Science Society of America Journal*, 41(2): 278-285, 1977.

Appendix A

BATCH PROCEDURES

Batch tests were initially conducted using the non-labelled compounds; however, because of the very low K_d values that were encountered, the analytical uncertainty resulted in a high degree of scatter in the data and thus a high degree of uncertainty in the measured K_d values. The use of carbon-14 labelled compounds allows for analysis by scintillation counting procedures, resulting in greater analytical precision, particularly at low concentrations. The results of the stable batch tests for xylene will be included; however, the only reliable results were obtained using carbon-14 labelled benzene and toluene. Only the procedure for the labelled compounds is included here.

Batch sorption isotherms were determined by equilibrating aqueous solutions of the different carbon-14 labelled hydrocarbons with the sand. Approximately 60 g samples of the sediment were weighed into 60-mL glass crimp-top hypovials fitted with open-holed caps and teflon-lined septums. A 20 mL aliquot of simulated groundwater was added and agitated to eliminate air bubbles. At the onset of a sorption experiment, approximately 20 mL of the solution containing a particular hydrocarbon was quickly added to the vials containing the simulated groundwater and sand. This resulted in a solid to liquid ratio of 1.5:1. As controls, two hypovials not containing sand were also filled to determine the initial hydrocarbon concentration; one immediately before and the other after the addition of the hydrocarbon solutions to the sediment samples. The vials were immediately capped, leaving a minimum headspace to avoid vapour loss. The samples and controls were equilibrated at $10 \pm 0.5^\circ\text{C}$ for 48 hr, on an apparatus that inverted the sample tubes automatically every 1 min. Following equilibration, the sediments were removed from suspension by centrifugation (200 g, 15 min; providing a Stoke's equivalent settling radius of 0.3μ). In all the experiments, the quantities of sediment and water were determined gravimetrically.

To determine the concentration of hydrocarbons remaining in solution after equilibration, a constant volume of supernatant was syringed directly out of the hypovials and placed in scintillation cocktail. The concentration of each sample was determined as the average result of two duplicate determinations. The liquid scintillation counting procedures are described below.

For calculation purposes it was assumed that the difference between the initial solution concentration, taken as the mean of the two control concentrations, and the equilibrium supernatant concentration could be attributed entirely to sorption onto the sediment phase. To assess the accuracy of this assumption, samples of the hydrocarbon solutions were analyzed immediately

before and after the addition of the solutions to the control and sediment samples. These values were compared with the control concentrations after the equilibration period. Very small losses were observed, indicating that only minor errors were introduced by calculating the solid phase concentrations as described.

Appendix B

LABORATORY COLUMN PROCEDURES

Breakthrough curves for the organic solutes were measured under water-saturated, steady-flow conditions. A 10-cm long by 8.5 cm diameter glass column with stainless steel end plates was packed homogeneously with air-dried Borden sand. The stainless steel end-plates were designed to facilitate one-dimensional flow within the sand column and to obtain uniform and reproducible concentration fronts at the onset of each experiment. A schematic of the column design is shown in Figure A.1. A seal was created at each end of the column with an expanded O-ring seated between the glass column and the end-plates. A variable speed, four-channel Ismatic IP-4 peristaltic pump was used to maintain uniform flow rates throughout the experiments. Effluent solution was collected with an automated collection system. A schematic of the apparatus is shown in Figure A.2. The surfaces that contacted the tracer solution were made of Teflon, glass or stainless steel, thus avoiding sources or sinks for the solutes being analyzed.

Saturation of the column proceeded by passing CO₂ gas through the column until the air was displaced, followed by slowly wetting the column from the bottom with the equilibrating solution. The saturated column was then flushed with equilibrating solution for several days to allow the pore-water chemistry to stabilize. Pulse-input experiments in which a small volume of tracer was injected over a one minute period were used. These experiments proceeded by simultaneously injecting chloride as the conservative tracer and the organic solutes as non-labeled compounds. The laboratory column experiments were conducted at $23 \pm 1^\circ\text{C}$. The concentration of each of the organic solutes in the injected solution was approximately 10 mg/kg.

To conduct an experiment, a glass syringe filled with tracer solution was connected to a line leading to a 3-way valve, the valve was opened to the input line, and the solution was injected into the influent end-plate over a one minute period. After the injection was complete, flow of the nontracer solution was resumed.

The effluent was sampled at precise time intervals with an automated switching valve (Scanivalve) which was connected to twelve sampling ports. Each port was constructed of a feed line that connected to a sampling head which in turn was clamped to a 10 mL hypovial. A small Viton o-ring was used to maintain a tight seal between the sampling head and the hypovial. Column effluent was fed into the automated switching valve and, in turn, into the sample vials. Displaced air and excess sample volume were allowed to escape through an overflow line which was attached to the sampling head. As each

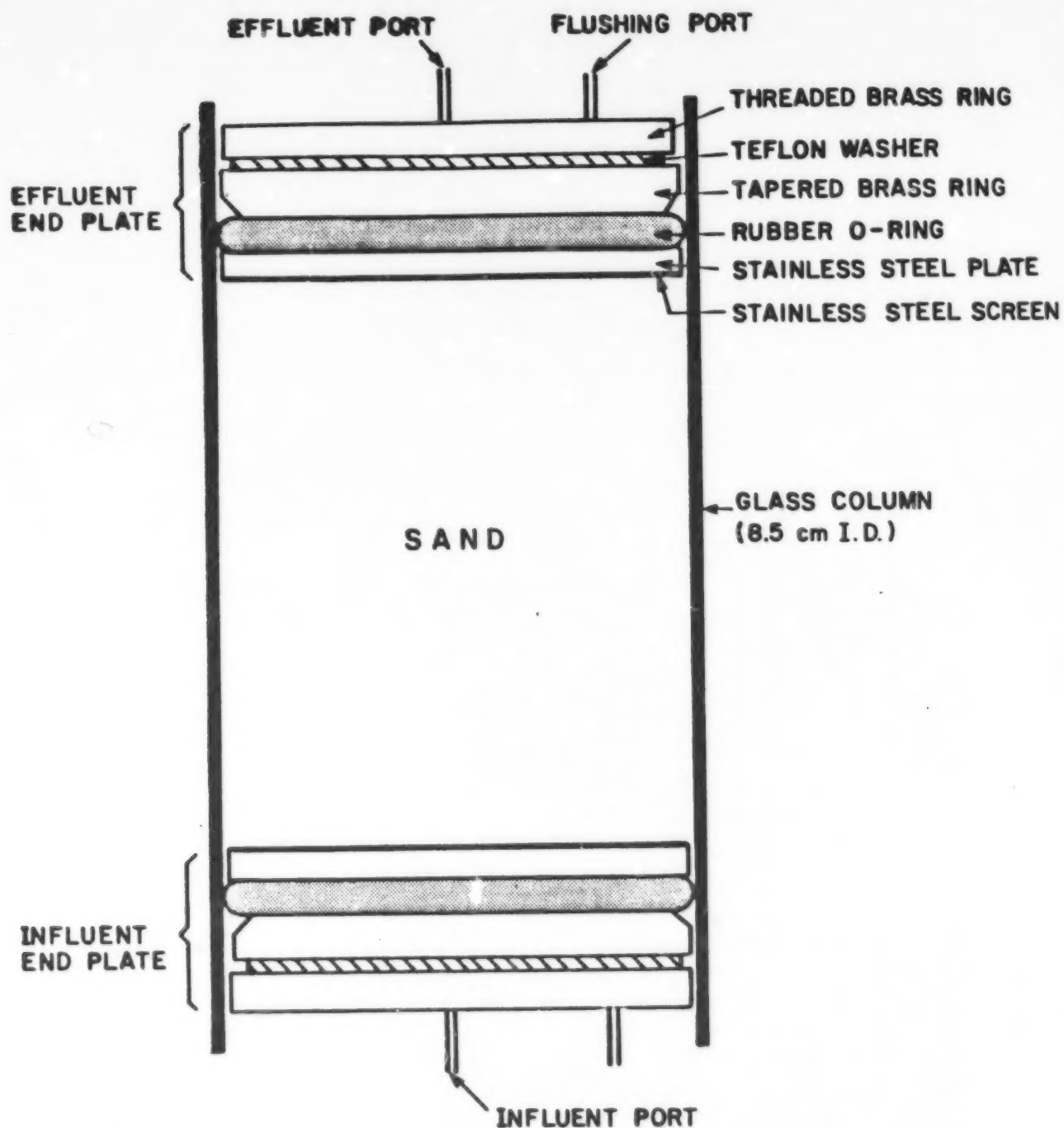


Figure B.1: Schematic of the column used in the laboratory experiments.

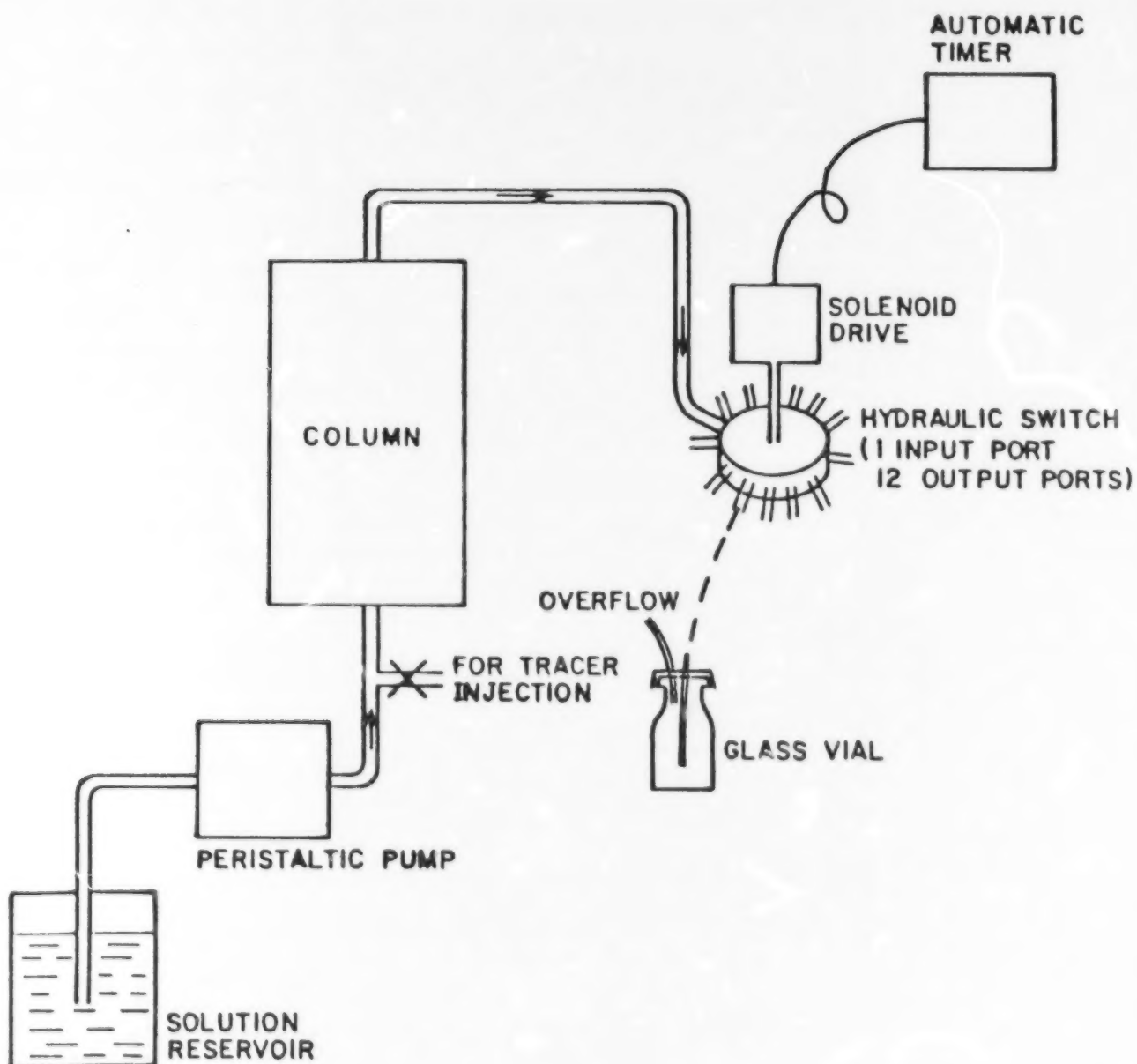


Figure B.2: Schematic of the laboratory column apparatus.

hypovial was filled, a known volume of effluent (5-10 mL) was allowed to overflow into the overflow line and collection vial to provide an additional barrier between the sample and the atmosphere. As the last sample in a round was collected, the sampling head at each port was removed, and the sample was quickly sealed with a teflon-lined septum.

Appendix C

IN-SITU COLUMN PROCEDURES

The field column experiments were conducted near the injection zone for the natural-gradient tracer experiment. The column device was constructed of a stainless steel split-spoon sampler fitted with a screened end-plate, injection and sampling lines, and a screened injection port mounted along a knife edge. A diagram of the device is shown in Fig. A.3 and is a modification of the device described by Goodwin and Gillham (1980). The device was attached to drill rods, lowered into a hole augered to the water table and then driven until it was filled to the screened end-plate with sediment. The tester was completely sealed except for the opening at the bottom, through which groundwater could flow vertically.

To conduct the experiments, groundwater was pumped through the column of sediment with a peristaltic pump attached to the sampling line. When a stable flow rate and specific conductance were obtained, a 10 mL volume of groundwater spiked with a small amount of chloride as a conservative tracer was introduced through the injection line to the screened port along the knife edge and thus into the moving groundwater. A flow-through conductance cell connected to a chart recorder was used to monitor the arrival of the conservative tracer in the outflow from the column. This information was used to determine if the device had been properly installed and for determinations of effective porosity.

For the reactive tracer breakthrough experiments, 10 mL of groundwater spiked with the test compounds and a conservative tracer was injected into the flow field in the same manner. As in the laboratory column experiments, the concentrations of each of the organic solutes in the injection solution was approximately 10 mg/kg (ppm). The materials used in the tester were stainless steel and Teflon, excluding a short length of flexible Viton tubing that passed through the peristaltic pump. Sampling of the effluent from the tester was accomplished in the same manner as in the laboratory column experiments. The samples were analyzed by gas chromatography as described below.

IN-SITU COLUMN METHOD

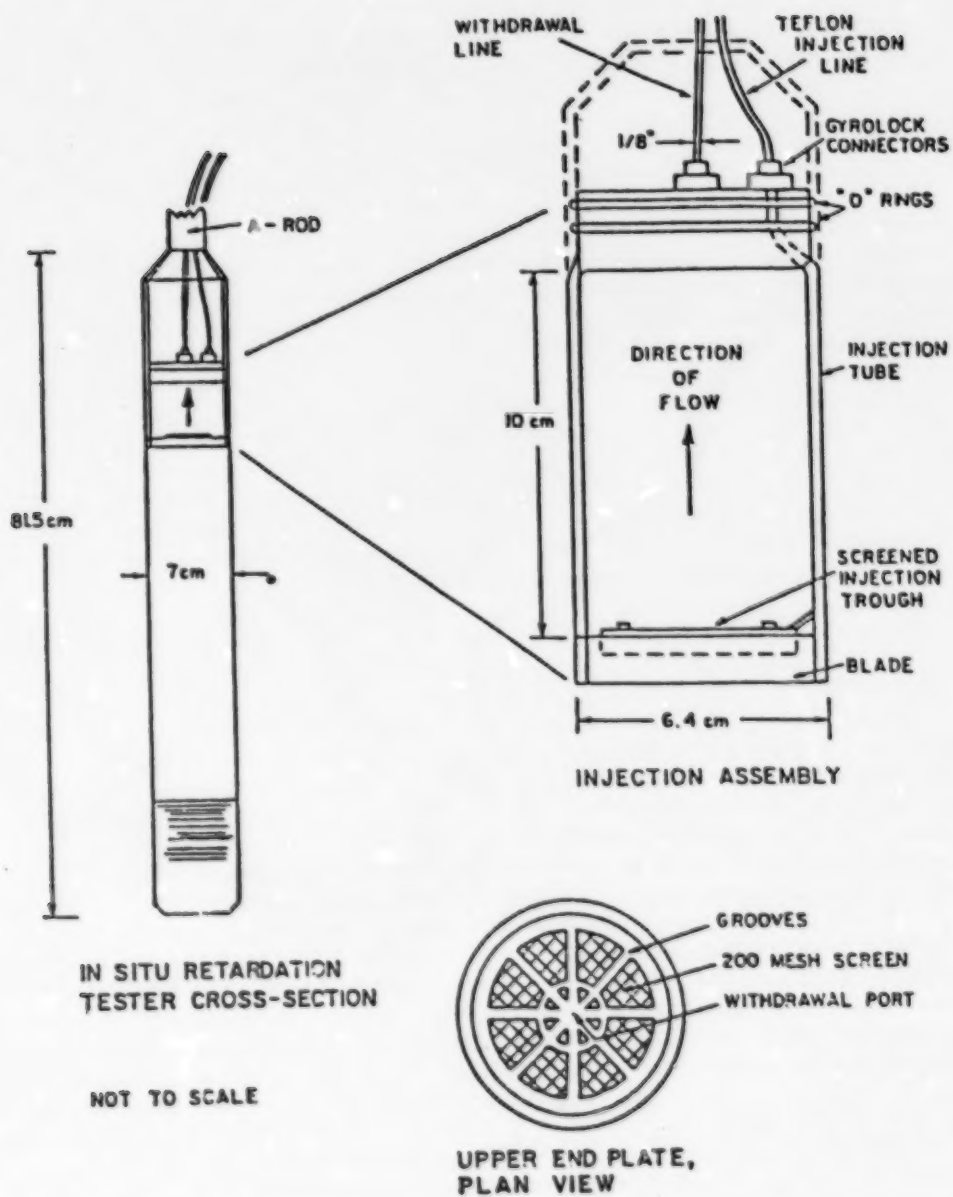


Figure C.1: Schematic of the field column device.

Appendix D

HEXANE MICRO-EXTRACTION FOR THE DETERMINATION OF PURGEABLE AROMATICS IN GROUNDWATER

A hexane liquid-liquid micro-extraction/gas chromatographic technique has been devised as a rapid alternative to the slower purge and trap and conventional solvent extraction methods for the determinations of benzene, toluene, and the three xylene isomers at trace levels in groundwater. Split injection isothermal capillary column chromatography permits a run time of five minutes without the loss of baseline resolution. Method detection limits in $\mu\text{g/L}$ are as follows: benzene, 1.8; toluene, 1.4; p-xylene, 0.6; m/xylene, 0.8; o-xylene, 1.2. Replicate analyses of an in-house quality control standard containing approximately 85 $\mu\text{g/L}$ of each compound were accumulated during a typical 8 day session. The means of the determinations differed no more than 1% from the true values with relative standard deviations averaging 2.9% overall. Evaluation of a USEPA quality control standard spiked into a typical organic-free groundwater matrix gave similar results.

D.1 Introduction

This paper describes a gas chromatographic technique to analyze groundwater samples for several aromatic components of gasoline, namely: benzene, toluene, and the p,m,o-xylenes. The samples analyzed were recovered from a controlled field injection experiment where possible interferents were known not to be present in the aquifer. Normally these compounds would be determined by purge and trap techniques (1). However, because the hydrogeologist may require many analyses to define the shape, movement and attenuation of a trace contaminant plume, purge and trap methods are too time consuming to use on a routine basis. Separatory funnel or continuous solvent extraction techniques are not only slow and labour intensive but may suffer from volatilization losses as well. The methodology presented here was derived from a pentane liquid-liquid extraction (LLE) technique previously described by Glaze et al., which requires that the partitioning of an analyte be at equilibrium between the two phases as opposed to being exhaustively extracted from the water (2). Pentane was replaced with hexane since the chromatographic column used easily affords complete separation of the analytes from the solvent peak. This helps to reduce the solvent vapour pressure in the sample vials thereby improving the precision of the method.

It was also found that the problem of analyte biodegradation in the field samples during storage is minimized by the addition of sodium azide at the time of collection.

D.2 Experimental

APPARATUS. Samples and aqueous standards are extracted in Supelco 10 ml crimp-top hypo-vials (actual volume = 18 ml) with teflon-faced silicone septa. The determinations are performed on a gas chromatograph equipped with a split injection port, capillary column, and FID. The column used is a 0.32mm x 6m fused quartz type with a 0.25 μ m bonded CARBOWAX 20M stationary phase. The chromatographic conditions are as follows: injection port temperature: 200°C; oven temperature: 90°C; detector temperature: 300°C; carrier gas: Helium; column flow rate: 5 ml/min.

REAGENTS. The following reagents are required: glass distilled hexane and methanol; organic-free reagent water; 10% aqueous sodium azide solution; reagent grade benzene, toluene, m-fluorotoluene, p,m,o-xylenes.

PROCEDURE. SAMPLE BOTTLE PREPARATION. Bottles and other glassware are soaked in a commercial alkaline cleaning solution for several hours, then rinsed with deionized water, dilute nitric acid, and more deionized water. The bottles are then baked overnight at 110°C. Upon removal from the oven, the bottles are covered with foil. Because the septa can be a major source of contamination, they must be boiled in water for one hour, then baked overnight at 110°C as well.

SAMPLE COLLECTION AND HANDLING. Sample vials are filled to overflowing with no aeration, quickly crimped, then stored on ice until needed. Prior to capping, 100 μ l of the sodium azide preservative is injected directly into the water. The same treatment is given to the aqueous standards.

To solvent extract a sample or standard, a vent needle is inserted through the septum, then one ml of water is removed with a syringe. With the vent still in place, 500 μ l of hexane, containing the internal standard m-fluorotoluene, is added. The vent is then removed and the bottle is agitated on its side at maximum speed on a platform shaker for 10 min. The bottle is inverted and the phases allowed to separate for 10 to 30 more minutes before the sample is analyzed.

The bottle is then righted and approximately 4 μ l of the hexane phase is removed, while venting, for injection into the chromatograph.

QUALITY CONTROL. The laboratory temperature is maintained at 22 $\pm$ °C. Samples and standards are equilibrated to this temperature before extraction.

The gas chromatograph is calibrated at the start of each working day by averaging the runs for three standard replicates at approximately 3000 μ g/L for each compound.

Two stock standards, one approximately an order of magnitude more concentrated than the other, are independently prepared. The higher concentration is used to calibrate the instrument; the lower one is used as a check, and is routinely run after every tenth sample. The standard checks are initially prepared at several concentrations in water to establish linearity and detection limits. Subsequently, during a sampling session they are run at a fixed concentration comparable to that of the unknowns.

A stock standard is prepared gravimetrically, injecting the various pure compounds through a septum into one 60 ml aliquot of methanol. This solution is then further diluted volumetrically by injecting through a septum into one litre of reagent water. An upper limit of 1% (v/v) methanol in water has been previously recommended; however, it was not necessary to exceed 0.05% for the present study (2). The aqueous standard dilution is mixed on a magnetic stirrer to avoid aeration, and then quickly distributed into hypo-vials with an all-glass and teflon repipette. The methanolic standards are stored in a freezer when not in use and discarded after 3 months. Aqueous standards are stored no longer than two days. The hexane extraction solution and reagent water blanks are run on a daily basis.

D.3 Results and Discussion

METHOD DETECTION LIMIT (MDL). Table I shows detection limits for the analytical procedure. It does not take into account field sampling errors, sample matrix, or analyte losses due to long term volatilization. These values were determined by the procedure recommended by USEPA/EMSL which defines MDL as the minimum concentration measurable with 99% confidence that it is greater than zero (3).

ACCURACY AND PRECISION. Near the detection limit, it can be seen that for the five compounds, the average absolute error is approximately $\pm 13\%$. The overall standard deviation at this level is 9.4%.

Table II summarizes the results of replicate analyses of in-house quality control samples accumulated during a typical sampling session (approximately 8 days in duration, $n = 31$). As was expected, at these higher concentrations the overall standard deviation has improved to 2.9%, while accuracy is virtually 100%.

To further evaluate the method, and its applicability to field samples, a USEPA quality control standard (WP 879 #1) was analyzed in a typical groundwater matrix. Calibration standards were prepared as previously described using laboratory reagent water. The results shown in Table III display standard deviations comparable to those obtained previously with errors which are generally larger, but still acceptable. It is quite likely that this increase in error is more a result of experimenter bias than matrix effects, as the ionic strength of the groundwater used is much lower than the 1.0 required to affect extraction efficiencies while the pH is fairly neutral (1).

D.4 Conclusions

The hexane micro-extraction method has a sensitivity approaching that of a purge and trap system, but can be used routinely, with a much shorter turnaround time. This allows the analyst to work with larger batches of samples at a faster rate. An obvious application of the technique would be in the monitoring of rapid compound biodegradation processes. The use of two chromatographs in tandem reduces run times even further.

Detection limits are adequate with a simple split injection, eliminating the need to employ more elaborate splitless or cryogenic schemes. These limits can be lowered somewhat by increasing the water to hexane ratio.

The column used is capable of resolving the p- and m- xylene isomers in a 5 minute isothermal run (see figure 1). Separation of these two isomers is impossible with the less polar capillary columns commonly employed. Furthermore, the method can easily be extended to include ethylbenzene and various halogenated aromatics.

The technique has been assessed as being suitable for water matrices with no interferences. Its applicability, however, to highly contaminated wastewater or landfill leachate remains to be demonstrated.

D.5 Acknowledgements

The author thanks Shirley Chatten, Guy Patrick, and Carol Ptacek for their technical assistance and Jim Barker for reviewing the manuscript.

D.6 References

- (1) "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater", EPA-600/4-82-057; Longbottom, James E., Lichtenberg, James J., Eds.; USEPA/EMSL: Cincinnati, OH, 1982; Method 602.
- (2) Glaze, William H., Lin, C.-C., Burleson, J.L.; Henderson, J.E., Mapel, D., Rawley, R., Scott, D.R., "Optimization of Liquid-Liquid Extraction Methods for Analysis of Organics in Water", Project Report, Contract No's. CR-805472, CR-808561; USEPA/EMSL: Cincinnati, OH, 1983.
- (3) "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater", EPA-600/4-82-057; Longbottom, James E., Lichtenberg, James J., Eds.; USEPA/EMSL: Cincinnati, OH, 1982; Appendix A.

Figure D.1: Typical sample chromatogram. Conditions described in text.

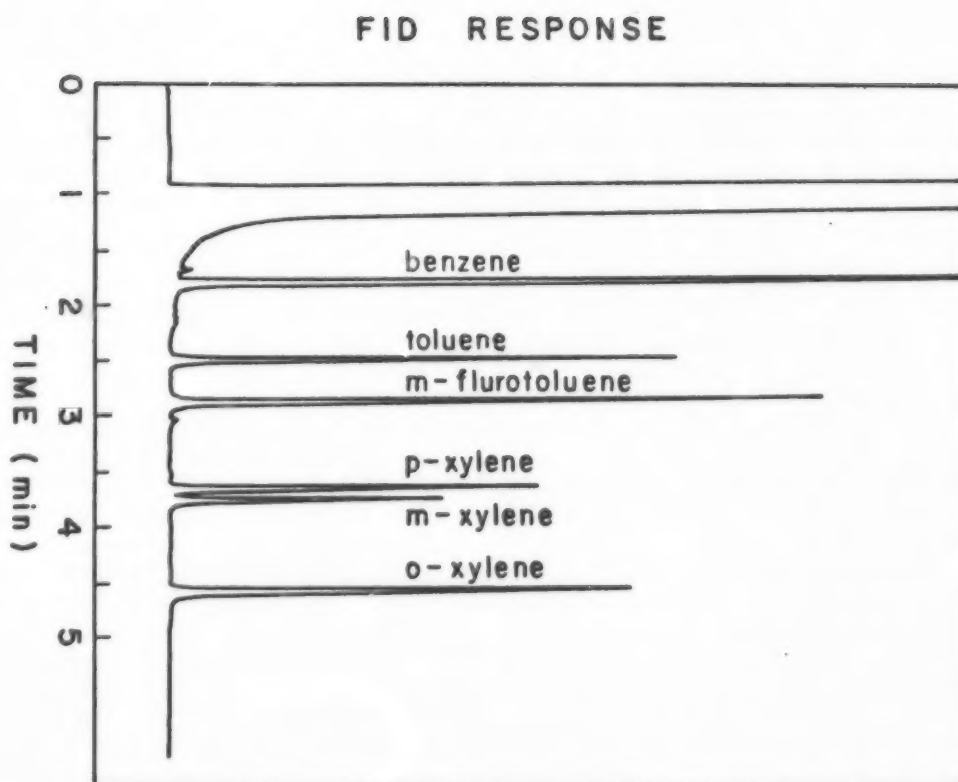


TABLE I. METHOD DETECTION LIMIT

ug/L						
Compound	N	S%	X	X ₀	E%	MDL
benzene	7	13	4.3±0.7	3.7	+16	1.8
toluene	7	13	3.2±0.5	3.6	-11	1.4
p-xylene	7	5.8	3.1±0.2	3.6	-14	0.6
m-xylene	7	5.7	4.4±0.3	3.7	+19	0.8
o-xylene	7	9.7	3.8±0.4	3.7	+3	1.2

N: number of replicate determinations; S%: relative standard deviation; X: mean of replicate determinations, 99% confidence level, background subtracted; X₀: true value; E%: average relative error; reagent water matrix.

TABLE II. ACCURACY AND PRECISION AT TYPICAL SAMPLE CONCENTRATIONS

ug/L

Compound	N	S%	X	X ₀	E%
benzene	31	4.2	84.5 $\pm$ 1.9	85.2	-1
toluene	31	2.9	83.8 $\pm$ 0.9	83.7	0
p-xylene	31	2.4	83.3 $\pm$ 1.5	83.5	0
m-xylene	31	2.8	86.2 $\pm$ 1.5	85.6	+1
o-xylene	31	2.0	86.6 $\pm$ 1.6	85.7	+1
reagent water matrix					

TABLE III. ANALYSIS OF USEPA QUALITY CONTROL SAMPLE WP 879 #1

ug/L

Compound	N	S%	X	X ₀	E%
benzene	7	3.0	30.6 $\pm$ 1.1	30.7	0
toluene	7	6.1	5.6 $\pm$ 0.4	4.1	+37
p-xylene	7	1.8	20.5 $\pm$ 0.4	19.1	+7
m-xylene	7	1.7	45.3 $\pm$ 0.9	42.6	+6
o-xylene	7	2.5	12.1 $\pm$ 0.4	10.6	+14

X₀: EPA value; groundwater matrix